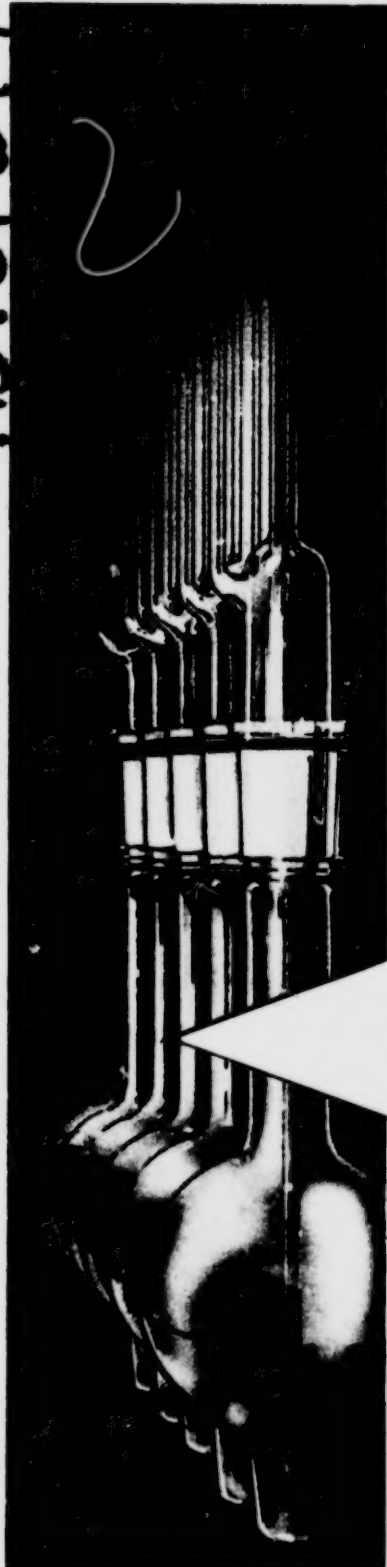


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SELECTED
METHODS
FOR THE
MEASUREMENT
OF AIR
POLLUTANTS

U. S. DEPARTMENT OF HEALTH,
EDUCATION, AND WELFARE
Public Health Service

**SELECTED METHODS
FOR THE
MEASUREMENT OF AIR POLLUTANTS**

Interbranch Chemical Advisory Committee

**U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Division of Air Pollution**

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio 45226

May 1965

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PREFACE

A mounting attack on the problems of air pollution has resulted from growing awareness of the steady degeneration of air quality due to our increasing urban population, greater industrial activity, and expanded transportation by automobiles and trucks. Methods of air analysis are basic tools required for studying pollution processes and effects, for monitoring the present degrees of pollution, for setting air quality standards, and for evaluating control efforts. This manual, addressed to the many chemists newly entering this work, is an effort to assist in the development of uniform standard methods of analysis. It provides a channel of communication making available the judgment and knowledge of a large group of chemists in the Public Health Service.

The methods for determination of pollutants of common interest presented herein were selected and presented in uniform format by experienced chemists on the staff of the Division of Air Pollution. The methods were critically reviewed by the Interbranch Chemical Advisory Committee, which is composed of representatives of the professional chemical groups in all branches of the Division. An effort was made to include all important details and provide references to the original literature for those needing more complete information.

We expect that these and similar methods will be subjected to rigorous testing procedures by collaborating laboratories having the confidence of most groups and that they will be found to merit the status of standard methods. In this connection, we believe that the tests should examine the critical factors of gas absorption efficiency and the stability of both the absorbing reagent and the sample reaction products during the aeration of the sampling process and in the interval before analysis. An adequate test would involve sampling accurately prepared gas mixtures throughout the applicable concentration range, with realistic amounts of interfering substances, in a system free from adsorption losses, such as a flow dilution system. Such testing will be time consuming. In the interim, this manual provides selected analytical methods as working tools representing the best judgment of our staff, on the basis of our experiences with them and the reports received from others.

The manual was edited by Messrs. Mario Storlazzi and Seymour Hochheiser. The name of the chemist who selected and prepared each procedure is indicated at its close. The members of the Interbranch Chemical Advisory Committee are Dr. A. P. Altshuller, Mr. Gilbert L. Gontner, Mr. Thomas R. Hauser, Mr. Seymour Hochheiser, Mr. Charles Punte, Dr. Bernard E. Saltzman, Mr. Stanley F. Sleva, Mr. Mario Storlazzi, and Mr. Elbert C. Tabor. Assistance from many other staff members is gratefully acknowledged.

At appropriate times new procedures will be added to this collection, and the present ones will be revised. Corrections and constructive criticism are welcomed.

Bernard E. Saltzman, Ph. D.
Chairman, Interbranch Chemical
Advisory Committee

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ABSTRACT

This manual is an effort to assist in the development of uniform standard methods of analysis of air pollutants. It makes available the judgment and knowledge of a large group of chemists in the Public Health Service. Methods of determining pollutants of common interest are presented in uniform format by chemists on the staff of the Division of Air Pollution. The methods were critically reviewed by the Interbranch Chemical Advisory Committee, which is composed of representatives of the professional chemical groups in all branches of the Division. Methods presented are as follows: For determination of sulfur dioxide, the West and Gaeke and the hydrogen peroxide methods; for determination of nitrogen dioxide and nitric oxide, the Saltzman method; for determination of oxidants, the neutral buffered-potassium iodide and the alkaline potassium iodide methods; for determination of aliphatic aldehydes, the 3-methyl-2 benzothiazolone hydrazone hydrochloride method; for determination of acrolein, the 4-hexylresorcinol method; for determination of formaldehyde, the chromotropic acid method; for determination of sulfate in atmospheric suspended particulates, the turbidimetric barium sulfate method; and for determination of nitrate in atmospheric suspended particulates, the 2,4 xylenol method.

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SELECTED METHODS FOR THE MEASUREMENT OF AIR POLLUTANTS

Determination of Sulfur Dioxide: West and Gaeke Method^{*}

INTRODUCTION

The West and Gaeke method is applicable to the determination of sulfur dioxide in outside ambient air in the concentration range from about 0.005 to 5 parts per million (ppm). Sulfur dioxide in the air sample is absorbed in 0.1 M sodium tetrachloromercurate.¹ Nonvolatile dichlorosulfitomercurate ion is formed in this process. Addition of acid-bleached pararosaniline and formaldehyde to the complex ion produces red-purple pararosaniline methylsulfonic acid, which is determined spectrophotometrically.² The system obeys Beer's Law up to about 10 μ l of sulfur dioxide per 10 ml of absorbing solution. This method is more sensitive than the hydrogen peroxide method and is not subject to interference from other acidic or basic gases or solids such as SO₃, H₂SO₄, NH₃, or CaO; however, the analysis should be completed within 1 week after sample collection, and the concentrations of ozone and nitrogen dioxide should be less than that of the sulfur dioxide.

REAGENTS

All chemicals used must be ACS analytical-reagent grade.

Absorbing reagent, 0.1 M sodium tetrachloromercurate. Dissolve 27.2 g (0.1 mole) mercuric chloride and 11.7 g (0.2 mole) sodium chloride in 1 liter of distilled water. (CAUTION: Highly poisonous. If spilled on skin, flush off with water immediately.)

Pararosaniline hydrochloride (0.04%), acid bleached. Dissolve 0.20 g of pararosaniline hydrochloride in 100 ml of distilled water and filter after 48 hours. This solution is stable for at least 3 months if stored in the dark and kept cool. The pararosaniline hydrochloride used should have an assay of better than 95% and an absorbance maximum at 543 or 544 m μ . Pipette 20 ml of this into a 100-ml volumetric flask. Add 6 ml of concentrated HCl. Allow to stand 5 minutes, then dilute to mark with distilled water. This solution should be pale yellow with a greenish tint. It can be stored at room temperature in an amber bottle for a week or for about 2 weeks if refrigerated.

* Prepared by Seymour Hochheiser, Technical Assistance Branch, Division of Air Pollution, Public Health Service. Approved by the Interbranch Chemical Advisory Committee, November 1963.

Formaldehyde, 0.2%. Dilute 5 ml of 40% formaldehyde to 1,000 ml with distilled water. Prepare weekly.

Standard sulfite solution. Dissolve 640 mg sodium metabisulfite (assay 65.5% as SO_2) in 1.0 liter of water. This yields a solution of approximately 0.40 mg/ml as SO_2 . The solution should be standardized by titration with standard 0.01 N I_2 by using starch as indicator, and adjusted to 0.0123 N. Then 1 ml = 150 μl SO_2 (25°C, 760 mm Hg). Prepare and standardize freshly.

Starch solution (iodine indicator), 0.25%. Make a thin paste of 1.25 g of soluble starch in cold water and pour into 500 ml of boiling water while stirring. Boil for a few minutes. Store in a glass stoppered bottle.

Standard iodine solution, 0.01 N. Dissolve 12.69 g of resublimed iodine in 25 ml of a solution containing 15 g of iodate-free KI; dilute to the 1,000-ml mark in a volumetric flask. Pipet exactly 100 ml of this 0.1 N solution and dilute to 1,000 ml in a volumetric flask with 1.5% KI. This solution can be used as a primary standard if the weighing is carefully done or it can be checked against a standard thiosulfate solution. This solution should be stored in an amber bottle, refrigerated, and then standardized on the day of use.

APPARATUS

Absorber. An all-glass midget impinger (similar to that shown in Figure 3) or other collection device should be capable of removing SO_2 from an air sample by using 10 ml of absorbing reagent. (Among the suppliers of midget impingers are Ace Glass Company and Gelman Instrument Company.)

Air pump. The air pump should be capable of drawing 2.5 liters per minute through the sampling assembly.

Air-metering and flow control devices. These devices ought to be capable of controlling and measuring flows with an accuracy of ± 2 percent. The flow meter should be calibrated for variations in reading with temperature and pressure of the airstream so that the appropriate corrections can be applied.

Thermometer (or other temperature-measuring device). This device should have an accuracy of $\pm 2^\circ\text{C}$.

Mercury manometer (or other vacuum-measuring device). This device should have an accuracy of 0.2 in. Hg.

Spectrophotometer or colorimeter. This instrument should be capable of measuring color intensity at 560 $\text{m}\mu$, in 1-cm absorbance cells or larger.

ANALYTICAL PROCEDURE

Collection of samples. Set up a sampling train consisting of, in order, absorber, trap to protect flow device, flow meter, flow control device, temperature and vacuum gauge, and air pump. Shield the

absorbing reagent from direct sunlight during and after sampling by covering the absorber with a suitable wrapping such as aluminum foil to prevent deterioration of sample. All probes and tubing upstream from the bubbler should be pyrex glass, stainless steel, or teflon. Butt-to-butt connections may be made with tygon tubing. The downstream metering device can be empirically corrected to atmospheric conditions by conducting a dummy run with an upstream flow meter in line that is open to the atmosphere.

Pipet exactly 10 ml of absorbing reagent into the absorber. Aspirate the air sample through the absorber at a rate of 0.2 to 2.5 liters per minute (depending upon the concentration of sulfur dioxide in the atmosphere and the sampling time desired). The sampling time may vary from a few minutes to 24 hours. For 24-hour sampling, the absorber selected should be capable of containing 20 ml or more of absorbing reagent. For best results, the sampling time and rate should be chosen to provide a concentration of approximately 2 to 4 μl of SO_2 in 10 ml of the absorbing reagent. The dichlorosulfito-mercurate formed may be stored for 3 days with only a slight decrease in strength (about 1 % per day). If samples are stored for longer periods, a correction factor should be applied.^{3,4} The sample may be stored in the collection device or transferred to a stoppered glass or polyethylene container.

Analysis. If a mercury precipitate is formed owing to the presence in the air sample of inorganic sulfides, thiols, or thiosulfates, it may be removed by filtration or centrifugation. To the clear sample, adjusted to 10 ml with distilled water to compensate for evaporative losses, add 1.0 ml of acid-bleached pararosaniline solution and 1.0 ml of the 0.2% formaldehyde solution and mix. In this analysis, reagent addition and spectrophotometric analysis can be automated.⁵

Treat a 10-ml portion of unexposed sodium tetrachloromercurate solution in the same manner for use as the blank. If the collecting reagent remains exposed to the atmosphere during the interval between sampling and analysis, the blank should be exposed in the same manner.

Allow 20 minutes for maximum color development and read the absorbance at 560 m μ in a spectrophotometer using the blank as the reference.

Calculations. Convert the volume of air sampled to the volume at standard conditions of 25°C, 29.97 in. Hg:

$$V_s = V \times \frac{(P - P_m)}{29.97} \times \frac{298.2}{(t + 273.2)} \quad (1)$$

V_s = volume of air in liters at standard conditions

V = volume of air in liters as measured by the meter

P = barometric pressure in inches of mercury

P_m = suction at meter in inches of mercury

t = temperature of sample air in degrees centigrade

Ordinarily the correction for pressure is slight and may be neglected.

Compute the microliters of sulfur dioxide in the sample by multiplying the absorbance by the slope of the calibration plot. Then the concentration is:

$$\text{ppm SO}_2 \text{ by volume} = \frac{\mu\text{l SO}_2}{V_s} \quad (2)$$

PREPARATION OF CALIBRATION CURVE

Pipet exactly 2 ml of standard sulfite solution into a 100-ml volumetric flask and dilute to mark with absorbing reagent. This final solution contains 3.0 $\mu\text{l SO}_2$ per ml.

Add accurately portions of the dilute standard sulfite solution of 0.5, 1.0, 1.5, and 2.0 ml to a series of 10-ml glass stoppered, graduated cylinders and dilute to the marks with absorbing reagent. Continue with the analysis procedure given above.

Plot the absorbance (optical density) as the abscissa against the $\mu\text{l SO}_2$ per 10 ml of absorbing solution on rectangular coordinate paper. Compute slope of straight line best fitting the data.

DISCUSSION OF PROCEDURE

The error for the combined sampling and analytical technique is $\pm 10\%$ in the concentration range below 0.10 ppm with increasing accuracy with concentration in the range 0.1 to 1 ppm. The measurements should be reported to the nearest 0.005 ppm at concentrations below 0.15 ppm and to the nearest 0.01 ppm above 0.15 ppm.

O_3 and NO_2 interfere if present in the air sample at concentrations greater than that of SO_2 .⁶ Interference of NO_2 is eliminated by including 0.06% sulfamic acid in the absorbing reagent.⁷ This may, however, result in losses of SO_2 during sampling and during storage of the sample for more than 48 hours after collection. NO_2 interference may also be eliminated by adding o-toluidine or sulfamic acid subsequent to sample collection.^{8,9}

Heavy metals, especially iron salts, interfere by oxidizing dichlorosulfitomercurate during sample collection. This interference is eliminated by including ethylenediaminetetraacetic acid in the absorbing reagent. Sulfuric acid or sulfate do not interfere. There is no experimental evidence to indicate that SO_3 interferes; it probably hydrolyzes preferentially in the absorbing reagent to form H_2SO_4 , rather than combines with sodium tetrachloromercurate to form the dichlorodisulfitomercurate complex ion. If the latter reaction prevails, the presence of SO_3 will result in a positive interference. If relatively large amounts of solid material are present, a filter may be used advantageously upstream; however, a loss of SO_2 may occur.

The color produced is independent of temperature in the range 11 to 30°C and is stable for 3 hours.¹

Much difficulty with the method has been caused by the use of impure pararosaniline hydrochloride.¹⁰ A commercial brand is now available that is specially selected for this procedure (Fisher Scientific Company, catalog No. P-389). The purity of the reagent may be estimated by comparing the slope of the calibration plot with the value 0.15 absorbance unit per μ l (obtained with 1-cm cells in a Cary spectrophotometer), which corresponds to a molar absorptivity of 36,700.

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Determination of Sulfur Dioxide: Hydrogen Peroxide Method*

INTRODUCTION

The hydrogen peroxide method is applicable to the determination of sulfur dioxide in outside ambient air in the concentration range from about 0.01 to 10.0 ppm.^{1,2} Sulfur dioxide in the air sample is absorbed in 0.03 N hydrogen peroxide reagent (adjusted to about pH 5). The stable and nonvolatile sulfuric acid formed in this process is titrated with standard alkali. The method requires only simple equipment and can be performed by analysts having lesser skills; it is preferable to the West and Gaeke method if sulfur dioxide is the principal acid or basic atmospheric gaseous pollutant, or if long storage of samples (longer than 1 week) is required prior to analysis.

REAGENTS

All chemicals used must be ACS analytical-reagent grade.

Absorbing solution, hydrogen peroxide, 0.03 N, pH 5. Dilute 3.4 ml of 30% hydrogen peroxide solution to 2 liters with distilled water. Determine the alkalinity of the solution by taking a 75-ml portion, adding 3 drops of mixed indicator, and adding approximately 0.002 N HCl or HNO₃ from a buret until the indicator turns pink (pH 5). Calculate the amount of acid necessary to adjust the acidity of the bulk of the absorbent and add the required amount. The zero blank, obtained by titrating 75 ml of the adjusted reagent with 0.002 N NaOH to the indicator equivalence point (green), should be not more than 2 drops. The reagent is stable at room temperature for at least 1 month.

Mixed indicator, 0.1%. Dissolve 0.06 g bromcresol green and 0.04 g methyl red in 100 ml of methanol. When stored in an amber bottle at room temperature, the reagent is stable for at least 6 months.

Standard sulfuric acid solution, 0.002 N. Prepare this solution by appropriate dilution of concentrated sulfuric acid. Standardize by the gravimetric barium sulfate method using a 200-ml portion, or with a primary standard such as Na₂B₄O₇ · 10 H₂O. This reagent may be stored indefinitely without change in strength.

Standard sodium hydroxide solution, 0.002 N. Prepare 2 liters of this solution by dilution of 1 N sodium hydroxide with freshly boiled (CO₂-free) distilled water. Standardize as follows: Pipet 25 ml of standard sulfuric acid solution into an Erlenmeyer flask, add 3 drops of mixed indicator solution, and titrate with the sodium hydroxide reagent contained in a buret to the green equivalence point. Store the reagent in a polyethylene or other alkali-resistant bottle and restandardize bi-monthly.

1 ml of 0.002 N NaOH = 64 µg SO₂ = 24.47 µl SO₂ (25°C, 760 mm Hg).

*Prepared by Seymour Hochheiser, Technical Assistance Branch, Division of Air Pollution, Public Health Service. Approved by the Interbranch Chemical Advisory Committee, November 1963.

APPARATUS

Absorber. A standard all-glass impinger or fritted bubbler (capacity about 300 ml is acceptable). (Among the suppliers are Corning Glass Company and Fisher Scientific Company.)

Air pump. The air pump should be capable of drawing 1 cfm through the sampling assembly.

Air-metering and flow control devices. These devices should be capable of controlling and measuring flows with an accuracy of $\pm 2\%$. The flow meter should be calibrated for variation in reading with temperature and pressure so that the appropriate corrections can be applied.

Thermometer (or other temperature-measuring device). This device should have an accuracy of $\pm 2^{\circ}\text{C}$.

Mercury manometer (or other vacuum-measuring device). This device should have an accuracy of 0.2 in. Hg.

Buret. The buret should have a 25- or 50-ml capacity graduated in 0.1-ml subdivisions, preferably with teflon plug, and should be capable of measuring volume with an accuracy of 0.05 ml.

ANALYTICAL PROCEDURE

Collection of samples. Set up a sampling train consisting of, in order, impinger, trap to protect flow device, flow meter, flow control device, temperature and vacuum gauge, and air pump. Measure 75 ml of absorbing reagent into the large impinger. Aspirate air through the bubbler at a rate of 1 cfm for 30 minutes. Note the readings of the vacuum gauge and thermometer. The downstream metering device can be empirically corrected to atmospheric conditions by conducting a dummy run with an upstream flow meter in line that is open to the atmosphere. If an integrated 24-hour air sample is desired, the sampling rate may be reduced to 1 liter per minute. For SO_2 concentrations of 0.3 ppm and greater, the strength of the standard alkali may be increased or the sampling time shortened. For concentrations of greater than 0.8 ppm, a second impinger should be connected in series so that a recovery efficiency of 98% is maintained. All probes and tubing upstream from the impinger should be pyrex glass, stainless steel, or teflon. Butt-to-butt connections may be made with short lengths of tygon tubing. The collected sample will not decompose on standing; consequently, the solution may be titrated long after sample collection. The sample may be stored in the impinger, which has been stoppered, or transferred to a stoppered glass or polyethylene container.

Titration. Add 3 drops of mixed indicator solution and titrate the solution with standard 0.002 N sodium hydroxide until the color changes from red to green. A reagent blank is titrated in the same manner and this result (which should be less than 0.1 ml) subtracted from the sample titer.

SELECTED METHODS

Calculations. Convert the volume of air sampled to the volume at standard conditions of 25°C, 29.97 in. Hg:

$$V_s = V \times \frac{P - P_m}{29.97} \times \frac{298.2}{t + 273.2} \quad (1)$$

V_s = volume of air in liters at standard conditions

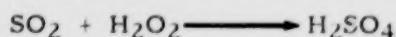
V = volume of air in liters as measured by the meter

P = barometric pressure in inches of mercury

P_m = suction at meter in inches of mercury

t = temperature of sample air in degrees centigrade

Results are computed on the basis of the following reaction:



Thus the net titer of 0.002 N NaOH (in ml) multiplied by 24.47 gives the microliters of sulfur dioxide. Then the concentration is:

$$\text{ppm SO}_2 \text{ by volume} = \frac{\mu\text{l SO}_2}{V_s} \quad (2)$$

DISCUSSION OF PROCEDURE

The error for the combined sampling and analytical technique is $\pm 10\%$ in the concentration range below 0.1 ppm with increasing accuracy with concentration in the range 0.1 to 1 ppm. The measurements should be reported to the nearest 0.01 ppm.

The presence in the air sample of strong acidic gases other than SO_2 or reactive acid solids such as HCl and NaHSO_3 gives erroneously high results whereas the presence of alkaline gases or reactive basic solids such as NH_3 and CaO gives erroneously low results. H_2SO_4 does not interfere, since it is not separated from the airstream appreciably, owing to its small particle size, except, perhaps, when the relative humidity is greater than 35%, which could result in particle sizes of greater than 1μ . SO_3 gas, if present, would be a positive interference. Sulfates do not interfere. CO_2 does not interfere since it is not absorbed in the acid-absorbing reagent. If relatively large amounts of solid material are present, a filter may be employed advantageously upstream; however, a loss of SO_2 may occur.³ The extent of this loss would depend upon the composition of the particulate matter and the nature and retentive capacity of the filter used. The acid-base indicator is not included in the absorbing reagent because it tends to decompose during sampling, resulting in unreproducible values.

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Determination of Nitrogen Dioxide and Nitric Oxide: Saltzman Method*

INTRODUCTION

The Saltzman method is intended for the manual determination of nitrogen dioxide in the atmosphere in the range of a few parts per billion (ppb) to about 5 ppm. Sampling is conducted in fritted bubblers. The method is also applicable to the determination of nitric oxide after it is converted to an equivalent amount of nitrogen dioxide by passage through a permanganate bubbler.³ Concentrations of both gases of 5 to 100 ppm may be sampled in evacuated bottles. The nitrogen dioxide is absorbed in Griess-Saltzman reagent.² A stable pink color is produced within 15 minutes and may be read visually or in an appropriate instrument. Only slight interfering effects occur from other gases.

REAGENTS

All reagents are made from analytical-grade chemicals in nitrite-free water prepared, if necessary, by redistilling distilled water in an all-glass still after adding a crystal each of potassium permanganate and of barium hydroxide. They are stable for several months if kept well stoppered in brown bottles in the refrigerator. The absorbing reagent should be allowed to warm to room temperature before use.

N-(1-Naphthyl)-ethylenediamine dihydrochloride, 0.1%. Dissolve 0.1g of the reagent in 100 ml of water. This is a stock solution.

Absorbing reagent. Dissolve 5 g of sulfanilic acid in almost a liter of water containing 140 ml of glacial acetic acid. Gentle heating is permissible, if desired, to speed up the process. To the cooled mixture, add 20 ml of the 0.1 % stock solution of N-(1-Naphthyl)-ethylenediamine dihydrochloride, and dilute to 1 liter. Avoid lengthy contact with air during both preparation and use, since this will result in discoloration of reagent because of absorption of nitrogen dioxide.

Standard sodium nitrite solution, 0.0203 g per liter. One ml of this working solution produces a color equivalent to that of 10 μ l of nitrogen dioxide (10 ppm in 1 liter of air at 760 mm of mercury and 25°C). Prepare fresh just before use by dilution from a stronger stock solution containing 2.03 g of the reagent grade granular solid (drying is unnecessary) per liter. The stock solution should be stable for 90 days.

Acid permanganate, used for nitric oxide determination. Dissolve 2.5 g of potassium permanganate in about 90 ml water, add 2.5 g of concentrated sulfuric acid (or 5.2 ml of 1:3 H₂SO₄) and dilute to 100 ml with distilled water. Prepare at frequent intervals, since the keeping quality is not good; discard when an appreciable precipitate of brown manganese dioxide is noted.

*Prepared by Bernard E. Saltzman, Laboratory of Engineering and Physical Sciences, Division of Air Pollution, Public Health Service. Approved by the Interbranch Chemical Advisory Committee, January 1964.

APPARATUS

Absorber. A specially ordered all-glass bubbler with a $60\text{-}\mu$ maximum pore diameter frit (Corning designation "coarse" or Ace designation "C"), similar to that illustrated in Figure 1, is used.

Acid permanganate bubblers. A midjet impinger with a nozzle about 1 mm in diameter and ground glass joints may be used (Figure 3). Accumulated deposits of manganese dioxide may be readily cleaned out by warming with a solution of hydroxylamine hydrochloride or oxalic acid.

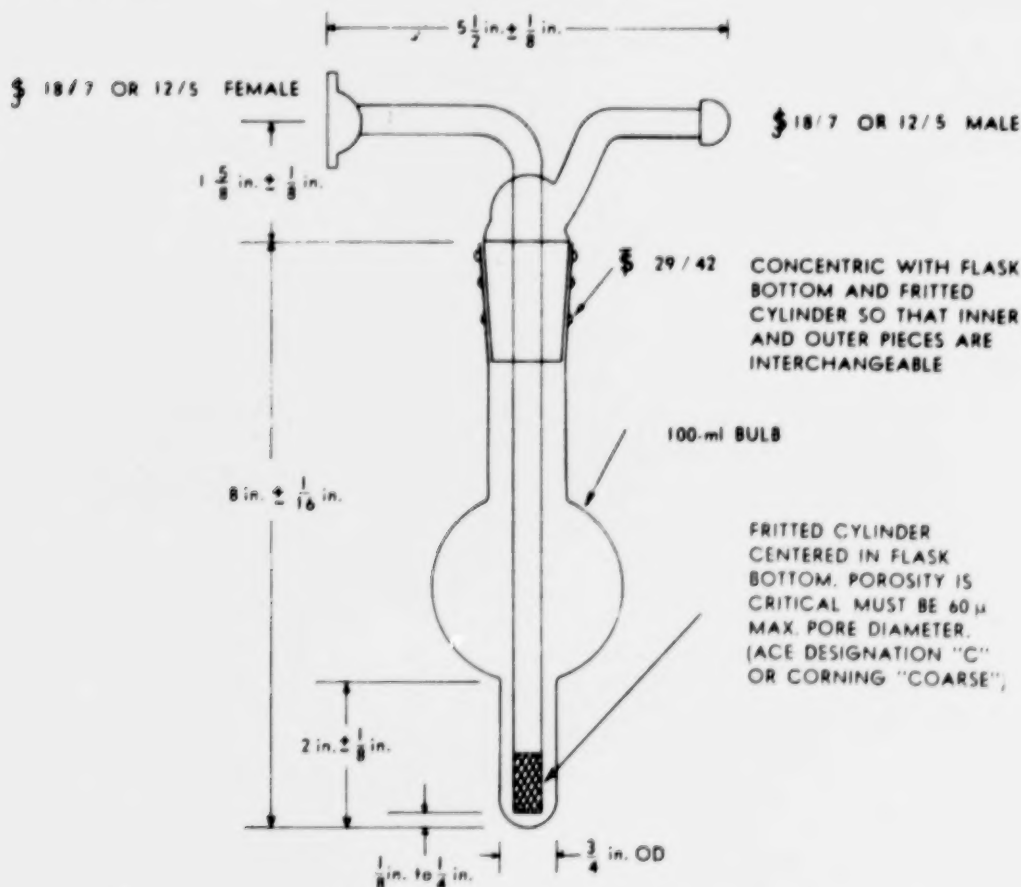


FIGURE 1. FRITTED BUBBLER FOR SAMPLING NITROGEN DIOXIDE.

Air-metering device. A glass rotameter capable of accurately measuring a flow of 0.4 liter per minute is recommended.

Air pump. An appropriate suction pump capable of drawing the required sample flow for intervals of up to 30 minutes is suitable. It is desirable to have a tee connection at the intake. The inlet connected to the sampling train should have an appropriate trap and needle valve (preferably of stainless steel). The second inlet should have a valve for bleeding in a large excess flow of clean air to prevent condensation of acetic acid vapors from the absorbing reagent, with consequent corrosion of the pump.

Spectrophotometer or colorimeter. A laboratory instrument suitable for measuring the pink color at 550 m μ , with stoppered tubes or cuvettes, is recommended.

ANALYTICAL PROCEDURE FOR NITROGEN DIOXIDE

Sampling train. Assemble, in order, a fritted absorber, rotameter, and pump. Use ground-glass connections upstream from the absorber. Butt-to-butt glass connections with slightly greased tygon or pure gum rubber tubing may also be used for connections without losses if lengths are kept minimal. Since the rotameter operates at an appreciable vacuum, make one dummy run to calibrate it against another rotameter or wet test meter installed upstream from the bubbler and operating at atmospheric pressure. If preferred, the sampling rotameter may be used upstream from the bubbler provided occasional checks are made to show that no nitrogen dioxide is lost. In either case, for accurate measurements, the rotameter must be kept free from spray or dust.

Sampling procedure. Pipet exactly 10 ml of absorbing reagent into the fritted bubbler. Draw an air sample through it at the rate of 0.4 liter (or less) per minute until sufficient color has developed (about 10 minutes). Note the total air volume sampled. If the sample air temperature and pressure deviate greatly from 25°C and 760 mm Hg, measure and record the values.

Determination. After collection or absorption of the sample, a direct red-violet color appears. Color development is complete within 15 minutes at ordinary temperatures. Compare with standards visually or transfer to stoppered cuvettes and read in a spectrophotometer at 550 m μ , using unexposed reagent as a reference. Colors may be preserved, if well stoppered, with only 3 to 4% loss in absorbance per day; however, if strong oxidizing or reducing gases are present in the sample in concentrations considerably exceeding that of the nitrogen dioxide, the colors should be determined as soon as possible to minimize any loss.

Standardization. Add graduated amounts of standard sodium nitrite solution up to 1 ml (measured accurately in a graduated pipet or small buret) to a series of 25-ml volumetric flasks, and dilute to marks with absorbing reagent. Mix, allow 15 minutes for complete color development, and read the colors.

Good results can be obtained with these small volumes of standard solution if they are carefully measured. If preferred, however, larger volumes may be used with correspondingly larger volumetric flasks.

Calculations. For convenience, standard conditions are taken as 760 mm of mercury and 25°C; thus, only slight correction by means of the well-known perfect gas equation is ordinarily required to get V, the standard volume of the air sample in liters. Quantities of nitrogen dioxide may be expressed as microliters, defined as V times the ppm nitrogen dioxide. It has been determined empirically that 0.72 mole

of sodium nitrite produces the same color as 1 mole of nitrogen dioxide; hence, 2.03 μ g of sodium nitrite is equivalent to 1 μ l of nitrogen dioxide.* The 1-ml standard is equivalent to 4 μ l of nitrogen dioxide per 10 ml of absorbing reagent.

Plot the absorbances of the standard colors, corrected for the blank, against the milliliters of standard solution. Beer's Law is followed. Draw the straight line giving the best fit and determine the slope (the value in milliliters of sodium nitrite intercepted at absorbance of exactly 1). This value multiplied by 4 gives the standardization factor, M, defined as the number of microliters of nitrogen dioxide required by 10 ml of absorbing reagent to give an absorbance of 1. For 2-cm cells the value was 3.65. Then:

$$\text{ppm nitrogen dioxide} = \text{corrected absorbance} \times M/V \quad (1)$$

If the volume of the air sample, V, is a simple multiple of M, calculations are simplified. Thus, for the M value of 3.65 previously cited, if exactly 3.65 liters of air is sampled through a bubbler, the corrected absorbance is also ppm directly. If other volumes of absorbing reagent are used, V is taken as the volume of air sample per 10 ml of reagent.

ANALYTICAL PROCEDURE FOR NITRIC OXIDE

Sampling for concentrations of 10 ppm and less. Assemble a sampling train composed of, in order, rotameter, fritted absorber, acid permanganate bubbler (with a nozzle rather than fritted inlet), fritted absorber, and pump. Pipet exactly 10 ml of absorbing reagent into each fritted absorber (first and third in the train). The second bubbler in the train should contain 10 ml of the acid permanganate solution, which may be reused several times. Draw an air sample through at a rate of 0.4 liter per minute (or less) until sufficient color has developed (about 10 minutes). After allowing an additional 15 minutes for full color development, the solution from the third bubbler may be read in the spectrophotometer and the nitric oxide computed. Colors too dark to read may be quantitatively diluted with unexposed absorbing reagent. If a simultaneous determination of nitrogen dioxide is desired it may be obtained by reading the colored solution from the first bubbler in a similar manner.

DISCUSSION OF PROCEDURES

Sampling efficiency. The porosity of the fritted bubbler is important, as well as the flow rate. An efficiency of 95% may be expected with a flow rate of 0.4 liter per minute and a maximum pore diameter of 60 μ . Considerably lower efficiencies are obtained with coarser frits, but these may be utilized if the flow rate is reduced. Since the quality control by some manufacturers is rather poor, it is desirable to measure the porosity of a new absorber experimentally as follows:

*Molar volume at 25°C, 760 mm Hg is 24.47 liters. Molecular weight $\text{NaNO}_2 = 69.00$; hence:

$$1 \mu\text{l NO}_2 = \frac{10^{-6}}{24.47} \text{ moles NO}_2 = \frac{10^{-6}}{24.47} \times 0.72 \times 69.00 = 2.03 \times 10^{-6} \text{ g NaNO}_2.$$

Carefully clean the apparatus with dichromate-concentrated sulfuric acid solution and rinse thoroughly with distilled water. Assemble the bubbler, add sufficient distilled water to cover the fritted portion, and measure the vacuum required to draw the first perceptible stream of air bubbles through the frit. The following equation is then used:

$$\text{maximum pore diameter } (\mu) = \frac{30 s}{P} \quad (2)$$

where s is the surface tension of water at the test temperature in dynes per cm (73 at 18°C, 72 at 25°C, and 71 at 31°C), and P is the measured vacuum in mm of Hg.

Nitrite equivalent of nitrogen dioxide. Standardization is based upon the empirical observation that 0.72 mole of sodium nitrite produces the same color as 1 mole of nitrogen dioxide. Using sodium nitrite is much more convenient than preparing accurately known gas samples for standardizing.

Efficiency of nitric oxide conversion. Conversion efficiency of nitric oxide to nitrogen dioxide by the permanganate bubbler may be commonly as low as 70%. This depends somewhat upon the quality of the permanganate solution and the design of the bubbler. Few data have been published on conversion efficiencies.

Conversion efficiencies of 95 to 100% have been reported recently¹ for an alternative method using a 17-mm OD glass U tube, containing one sheet of impregnated glass fiber paper cut into 1/4-in. strips, at a flow rate of 290 ml per minute. (A stack of 25 sheets of 7-cm-diameter paper is impregnated with 25 ml of 2.5% $\text{Na}_2\text{Cr}_2\text{O}_7$, 2.5% H_2SO_4 , and dried in a vacuum oven at 160°F, or on a hot plate at 200°F. Discard top and bottom sheets, store in closed bottle.) The useful life of the paper is limited, and it deteriorates rapidly when exposed to reagent vapors downstream from a bubbler. Hence a different sampling train, composed of rotameter, paper, fritted absorber, and pump, is used. The analysis yields the total of nitric oxide and nitrogen dioxide. A separate analysis of the latter gas must be made and deducted to give the concentration of nitric oxide.

Effects of interfering gases. A fivefold ratio of ozone to nitrogen dioxide will cause a small interference, the maximal effect occurring in 3 hours. The reagent assumes a slightly orange tint.

A 10-fold ratio of sulfur dioxide produces no effect. A 30-fold ratio slowly bleaches the color to a slight extent. The addition of 1% acetone to the reagent before use retards the fading by forming a temporary addition product with sulfur dioxide. This permits reading within 4 to 5 hours (instead of the 45 minutes required without the acetone) without appreciable interferences.

The interferences from other nitrogen oxides and other gases that might be found in polluted air are negligible.

SAMPLING RELATIVELY LARGE CONCENTRATIONS (MORE THAN 5 ppm) WITH EVACUATED BOTTLES

Grab-sample bottles. Ordinary glass-stoppered borosilicate glass bottles of 30- to 250-ml sizes are suitable if provided with a mating ground joint attached to a stopcock for evacuation. Calibrate the volume by weighing with connecting piece, first empty, then filled to the stopcock with distilled water.

Fifty- or one hundred-milliliter glass syringes are convenient (although less accurate) for moderately large concentrations.

Sampling for nitrogen dioxide. Sample in evacuated bottles of appropriate size (30 ml for up to 100 ppm, to 250 ml for down to 1 ppm) containing exactly 10 ml (or other convenient volume) of absorbing reagent. First grease the joint lightly with silicone or fluorocarbon grease. If a source of vacuum is available at the place of sampling, it is best to evacuate just before sampling to eliminate any uncertainty about loss of vacuum. A three-way Y stopcock connection is convenient. One leg is connected to the sample source, one to the vacuum pump, and the third to a tee attached to the bottle and to a mercury manometer or accurate gauge. In the first position of the Y stopcock, the bottle is evacuated to the vapor pressure of the absorbing reagent, and the actual vacuum is read. In the second position of the Y stopcock, the sampling bottle is closed and the vacuum pump draws air through the sampling line to flush it thoroughly. In the third position of the Y stopcock, the sampling line is connected to the evacuated bottle, and the sample is collected. The stopcock on the bottle is then closed. Allow 15 minutes with occasional shaking for complete absorption and color development. For calculation of the standard volume of the sample, the pressure is recorded as the difference between the filled and evacuated conditions, and the uncorrected volume is that of the bottle plus that of the connection up to the stopcock minus the volume of absorbing reagent.

Another, more convenient but less accurate field method for moderately large concentrations is to use 50- or 100-ml glass syringes. Ten ml of absorbing reagent is kept in the capped syringes, and 40 or 90 ml of air is drawn in at the time of sampling. The absorption of nitrogen dioxide is completed by capping and shaking vigorously for 1 minute, after which the air is expelled. Additional air may be drawn in and the process repeated several times if necessary to develop sufficient final color.

The syringe method is also useful when appreciable concentrations of nitric oxide are suspected. Interference caused by the air oxidation of nitric oxide to nitrogen dioxide is minimized by expelling the air sample immediately after the 1-minute absorption period.

Sampling for nitric oxide. Sample in an evacuated bottle containing absorbing reagent, as described in the procedure for nitrogen dioxide. Close the stopcock and allow sufficient time for the air oxidation of the nitric oxide to be substantially completed (Figure 2), shaking the bottle at intervals to prevent loss of nitrogen dioxide on the glass. Read the color in the manner previously described. The nitrogen dioxide initially present may be separately determined in a syringe and deducted if appreciable. The calculated concentration of nitric oxide may be corrected for incomplete conversion according to Figure 2.

Low conversions should be avoided for accurate results. A second correction for fading of the color (about 3% of the absorbance per day) may be made for a prolonged absorption period.

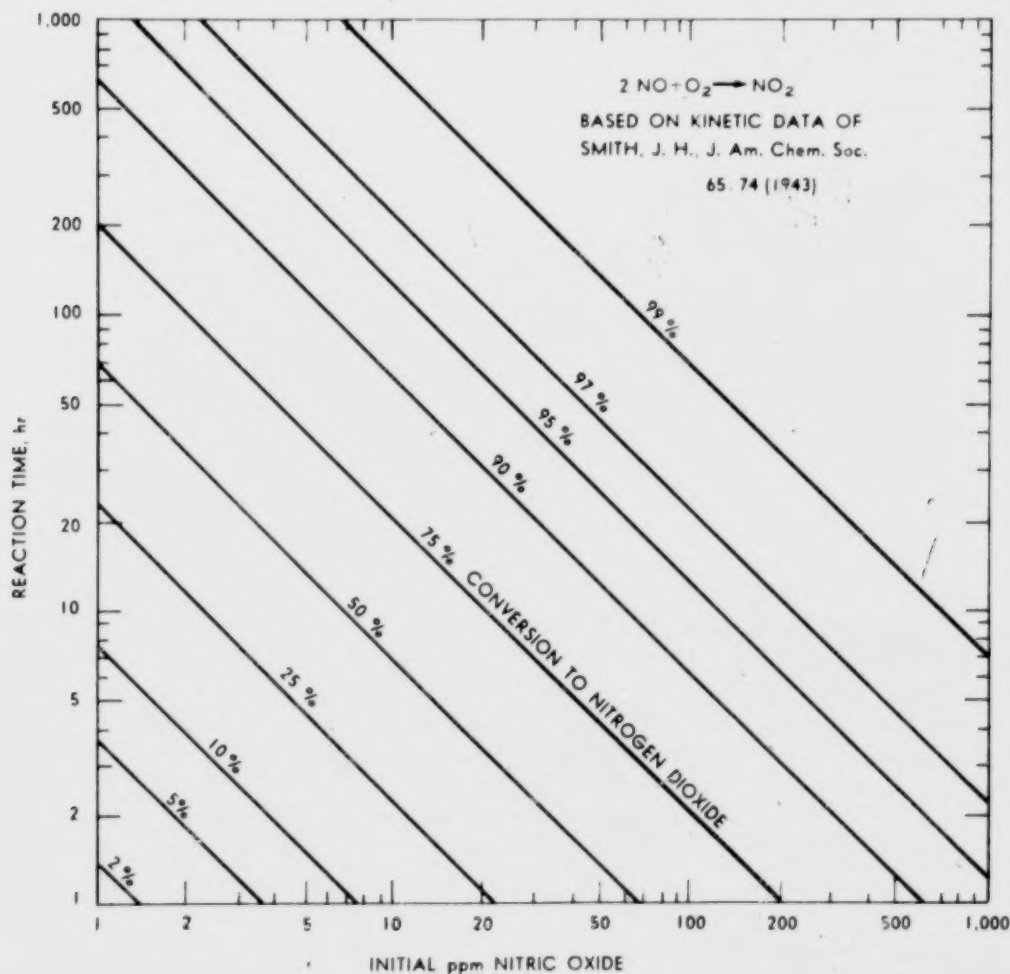


FIGURE 2. OXIDATION OF NITRIC OXIDE BY AIR AT 25°C.

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Determination of Oxidants (Including Ozone): Neutral Buffered-Potassium Iodide Method*

INTRODUCTION

This method^{1,2} is intended for the manual determination of oxidants (including ozone) in the range of a few parts per hundred million (pphm) to about 10 ppm. Ozone, chlorine, hydrogen peroxide, organic peroxides, and various other oxidants will liberate iodine by this method. A positive response of about 10% of the ppm nitrogen dioxide occurs. It is customary for convenience to express the results as ozone. The advantages of this procedure over the alkaline iodide procedure are simplicity, accuracy, and precision. The analysis must, however, be completed during the period of 30 minutes to 1 hour after sampling. Sampling is conducted in midjet impingers containing 1% potassium iodide in a neutral (pH 6.8) buffer composed of 0.1 M disodium hydrogen phosphate and 0.1 M potassium dihydrogen phosphate. Iodine is liberated in the absorbing reagent and measured in an appropriate instrument. Serious interfering effects occur from reducing gases and dusts.

REAGENTS

All reagents are made from analytical-grade chemicals. Traces of reducing impurities cause very serious errors.

Double-distilled water, used for all reagents. To distilled water in an all-glass still, add a crystal each of potassium permanganate and barium hydroxide, and redistill.

Absorbing reagent. Dissolve 13.61 g of potassium dihydrogen phosphate, 14.20 g of anhydrous disodium hydrogen phosphate (or 35.82 g of dodecahydrate salt), and 10.00 g of potassium iodide successively and dilute the mixture to exactly 1 liter. Age at room temperature for at least 1 day before using. This solution may be stored for several weeks in a glass stoppered brown bottle in the refrigerator, or for shorter periods at room temperature. Do not expose to sunlight.

Standard iodine solution, 0.05 N. Dissolve successively 16.0 g of potassium iodide and 3.173 g of iodine; make to a volume of exactly 500 ml. Age for at least 1 day before using. Standardization is unnecessary if the weighing is carefully done. (The solution may also be standardized by titration with sodium thiosulfate by using starch indicator.)

*Prepared by Bernard E. Saltzman, Laboratory of Engineering and Physical Sciences, Division of Air Pollution, Public Health Service. Approved by the Interbranch Chemical Advisory Committee, March 1964.

APPARATUS

Absorber. All-glass midget impingers with a graduation mark at 10 ml, similar to that shown in Figure 3, are used. (Other bubblers with nozzle or open-end inlet tubes may be used. Fritted bubblers tend to give comparatively low results.) Impingers must be kept scrupulously clean and dust free. All traces of grease must be removed by treatment with dichromate-concentrated sulfuric acid solution followed by tap and distilled water.

Air-metering device. A glass rotameter capable of measuring a flow of 1 to 2 liters per minute with an accuracy of $\pm 2\%$ is recommended.

Air pump. An appropriate suction pump capable of drawing the required sample flow for intervals of up to 30 minutes is suitable. It is desirable to have a trap on the inlet to protect the needle valve and pump against accidental flooding with absorbing reagent and consequent corrosion.

Spectrophotometer. A laboratory instrument suitable for measuring the yellow color at 352 m μ , with stoppered tubes or cuvettes (suitable for ultraviolet use), is recommended.

ANALYTICAL PROCEDURES

Collection of samples. Assemble a train composed of a midget impinger, rotameter, and pump. Use ground-glass connections upstream from the impinger. Butt-to-butt glass connections with slightly greased tygon tubing may also be used for connections without losses if exposed tubing lengths are kept minimal. Pipet exactly 10 ml of the absorbing solution into the midget impinger and sample at a flow rate of 1 to 2 liters per minute. Note the total volume of the air sample. If the sample air temperature and pressure deviate greatly from 25°C and 760 mm Hg, measure and record these values. Sufficient air should be sampled so that the equivalent of 0.5 to 10 μ l of ozone is absorbed. Sampling periods of longer than 30 minutes should be avoided. For a flow rate of 2 liters per minute, a 30-minute sample should yield a sensitivity of 0.01 ppm. Do not expose the absorbing reagent to direct sunlight.

Analysis. If appreciable evaporation has occurred, add distilled water to restore the volume to the 10-ml graduation mark. Transfer the exposed absorbing reagent (without diluting with rinse water) to a clean colorimeter tube or cuvette. During the period of 30 to 60 minutes after the sampling period, determine the absorbance at 352 m μ , using a tube or cuvette freshly filled with distilled water as the reference. A few additional readings at earlier and later times should be made occasionally when practicable to check on the color stability. Every few days, determine the blank correction (to be deducted from sample absorbances) by reading the absorbance of unexposed reagent.

Samples having a color too dark to read may be quantitatively diluted with additional absorbing reagent, and the absorbance of the diluted solution read. The dilution factor must then be introduced into the calculations.

Standardization. Freshly prepare 0.0025 N iodine standard by pipetting exactly 5 ml of the 0.05 N standard stock solution into a 100-ml volumetric flask and diluting to mark with absorbing reagent. Place 0.2-, 0.4-, 0.6-, and 0.9-ml portions (measured accurately in a graduated pipet or small buret) of the diluted standard iodine in separate 25-ml volumetric flasks and dilute to marks with absorbing reagent. Mix thoroughly. Immediately after preparation of this known series read the absorbance of each at 352 m μ in the usual manner.

Calculations. For convenience, standard conditions are taken as 760 mm of mercury and 25°C; thus, only slight correction by means of the well-known perfect gas equation is required to get V, the standard volume in liters of the air sampled. Ordinarily this correction may be omitted. Quantities, customarily expressed in terms of ozone, may be expressed as microliters, defined as V times ppm ozone. It has been determined empirically that 1 mole of ozone liberates 1 mole of iodine (I₂) by this procedure.

Plot the corrected absorbances of the standard colors against the exact calculated normalities of the corresponding diluted iodine solutions. Beer's Law is followed. Draw the straight line giving the best fit and determine the normality of iodine solution intercepted at an absorbance of exactly 1. This value multiplied by 1.224×10^5 * gives the standardization factor M, defined as the number of microliters of ozone required by 10 ml of absorbing reagent to give an absorbance of exactly 1. For 2-cm cells this value is 4.8.

Results for samples are computed as follows:

$$\text{ppm oxidant (expressed as O}_3\text{)} = \text{corrected absorbance} \times M/V \text{ (1)}$$

If the volume of the air sample V, is a simple multiple of M, calculations are simplified. Thus, for the M value of 4.8 previously cited, if exactly 4.8 liters of air are sampled through the impinger, the corrected absorbance is also ppm directly. If other volumes of absorbing reagent are used, V is taken as the volume of air sample per 10 ml of absorbing reagent.

DISCUSSION OF PROCEDURE

Sampling efficiency. When two impingers are placed in series, iodine will very rarely be liberated from the solution in the second absorber. Thus sampling efficiency is very high. Fritted bubblers, which also appear to have equally high sampling efficiencies, usually give, however, less iodine for a given amount of ozone and should not, therefore, be used. This is due to the complex chemistry of ozone in iodine solutions.²

* Standard molar volume (760 mm Hg, 25°C)=24.47 liters. Hence 1 μ mole I₂ = 24.47 μ l O₃, and 10 ml 1 N iodine = 5×10^3 μ mole I₂ = 1.224×10^5 μ l O₃.

Stability of colors. About 90% of the iodine is liberated by ozone immediately and the remaining 10% appears to be liberated by a single slow-reacting component (probably H_3PO_5 produced by the ozone in a side reaction) with a half-life of about 10 minutes. Thus the color will gradually increase until about 45 minutes after sampling, after which fading will begin. Good results are obtained by reading during the period of 30 to 60 minutes after sampling.

Oxidants other than ozone will also liberate iodine but at a slower rate. Some estimate of the presence of such materials or of fading due to reducing substances can be made for each situation by making occasional measurements over an extended period of time. Use of analytical-grade reagents and of carefully cleaned glassware reduces losses of iodine and fading processes. Do not expose the reagent to direct sunlight, since additional iodine may be released.

Comparison with 2% potassium iodide reagent. A similar reagent, containing 2% potassium iodide in the same buffer that has been adjusted to pH 7.0 with sodium hydroxide pellets, is in use.³ Both reagents should give comparable results. Color development as well as fading is slower in the 1% reagent, so that a longer time interval should be available for accurate reading.

Interferences. The negative interferences from reducing gases such as sulfur dioxide and hydrogen sulfide are very serious (probably on a mole-to-mole equivalency). The procedure is very sensitive to reducing dusts, which may be present in the air or on the glassware. Losses of iodine occur even on clean glass surfaces, and thus the manipulations should minimize this exposure.

Elimination of the interference of sulfur dioxide, even when it was present in as high as hundredfold ratio to oxidant, has been accomplished recently⁴ by incorporating an extra large (140-ml) absorbing U-tube in the sampling train upstream from the impinger. The absorbent, which removes sulfur dioxide without loss of oxidant, is glass fiber paper impregnated with chromium trioxide. (Drop 15 ml of aqueous solution containing 2.5 g chromium trioxide and 0.7 ml concentrated sulfuric acid uniformly over 60 in.² of paper, and dry in an oven at 80 to 90°C for 1 hour. Cut the paper into 1/4- x 1/2-in. strips, each folded once into a V-shape, pack into the U-tube, condition by drawing air through tube overnight.) The absorbent has a long life (at least 1 month). If it becomes visibly wet from sampling humid air, it must be dried (with dry air) before further use.

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Determination of Oxidants (Including Ozone): Alkaline Potassium Iodide Method*

INTRODUCTION

This method¹ is intended for the manual determination of oxidants (including ozone) in the range of a few pphm to about 20 ppm. Ozone, chlorine, hydrogen peroxide, organic peroxides, and various other oxidants will liberate iodine by this method. The response to nitrogen dioxide is limited to 10% by the use of sulfamic acid in the procedure to destroy nitrite. It is customary for convenience to express the results as ozone. The advantage of this procedure over the neutral iodide procedures is that a delay is permissible between sampling and completion of the analysis. Sampling is conducted in midjet impingers containing 1% potassium iodide in 1 N sodium hydroxide. A stable product is formed that can be stored with little loss for several days. The analysis is completed in a laboratory by addition of phosphoric-sulfamic acid reagent, which liberates the iodine. The yellow iodine color is read in an appropriate instrument. Serious interfering effects occur from reducing gases and dusts.

REAGENTS

All reagents are made from analytical-grade chemicals. They are stable for several months in well-stoppered bottles.

Double-distilled water, used for all reagents. Redistill distilled water in an all-glass still after adding a crystal each of potassium permanganate and barium hydroxide.

Absorbing reagent. Dissolve 40.0 g of sodium hydroxide in almost a liter of water, then dissolve 10.0 g of potassium iodide and make the mixture to 1 liter. Store in a glass bottle with a screw cap (with inert liner) or rubber stopper (previously boiled for 30 minutes in alkali and washed). Age for at least 1 day before using.

Acidifying reagent. Five g of sulfamic acid is dissolved in 100 ml of water, then 84 ml of 85% phosphoric acid is added, and the mixture is made to 200 ml.

Standard potassium iodate solution. Dissolve 0.758 g of potassium iodate in water and dilute to 1 liter. One ml of this stock solution is equivalent to 400 μ l of ozone. Prepare a dilute standard solution just before it is required by pipetting exactly 5 ml of stock solution into a 50-ml volumetric flask and making to mark with water.

*Prepared by Bernard E. Saltzman, Laboratory of Engineering and Physical Sciences, Division of Air Pollution, Public Health Service. Approved by the Interbranch Chemical Advisory Committee, March 1964.

APPARATUS

Absorber. All-glass midget impingers with a graduation mark at 10 ml, similar to that shown in Figure 3, are used. (Other bubblers with nozzle or open-end inlet tubes may be used. Fritted bubblers tend to give relatively low results.) Impingers must be kept scrupulously clean and dust free. All traces of grease should be removed by treatment with dichromate-concentrated sulfuric acid solution (cleaning solution) followed by tap and distilled water.

Air-metering device. A glass rotameter capable of measuring a flow of 1 to 2 liters per minute with an accuracy of $\pm 2\%$ is recommended.

Air pump. An appropriate suction pump capable of drawing the required sample flow for intervals of up to 30 minutes is suitable. It is desirable to have a trap on the inlet to protect the needle valve and pump against accidental flooding with absorbing reagent and consequent corrosion.

Spectrophotometer. A laboratory instrument suitable for measuring the yellow color at 352 m μ with stoppered tubes or cuvettes (suitable for ultraviolet use) is recommended.

ANALYTICAL PROCEDURES

Collection of samples. Assemble a train composed of a midget impinger, rotameter, and pump. Use ground-glass connections upstream from the impinger. Butt-to-butt glass connections with slightly greased tygon tubing may also be used for connections without losses if lengths are kept minimal. Pipet exactly 10 ml of the absorbing solution into the midget impinger and sample at a flow rate of 1 to 2 liters per minute. Note the total volume of the air sample. If the sample air temperature and pressure deviate greatly from 25°C and 760 mm Hg, measure and record these values. Sufficient air should be sampled so that the equivalent of 1 to 15 μ l of ozone is absorbed. If appreciable evaporation has occurred, add distilled water to restore the volume to the 10-ml graduation mark. If the analysis is to be completed later, transfer the solution, without rinsing, to a clean, dry, glass-stoppered, 25-ml, graduated cylinder (or a bottle) for storage. Prolonged storage may cause "freezing" of glass stoppers.

Analysis. Measure the volume of exposed absorbing reagent in a 25-ml, glass-stoppered, graduated cylinder. (Do not use rinse water in any transfers.) Add from a rapid (serological-type), graduated pipette exactly one-fifth of this volume of the acidifying reagent and mix thoroughly. Place the stoppered cylinder in a water bath at room temperature for 5 to 10 minutes to dissipate the heat of neutralization. Transfer a portion of the sample to a cuvette and determine the absorbance at 352 m μ with a cuvette containing distilled water as the reference. Do not delay the reading, since reducing impurities sometimes cause rapid fading of the color.

Prepare a reagent blank by adding 2 ml of the acidifying reagent to 10 ml of unexposed absorbing reagent. Cool and determine the blank absorbance. This blank absorbance should be determined each day and should be subtracted from the absorbances of the samples.

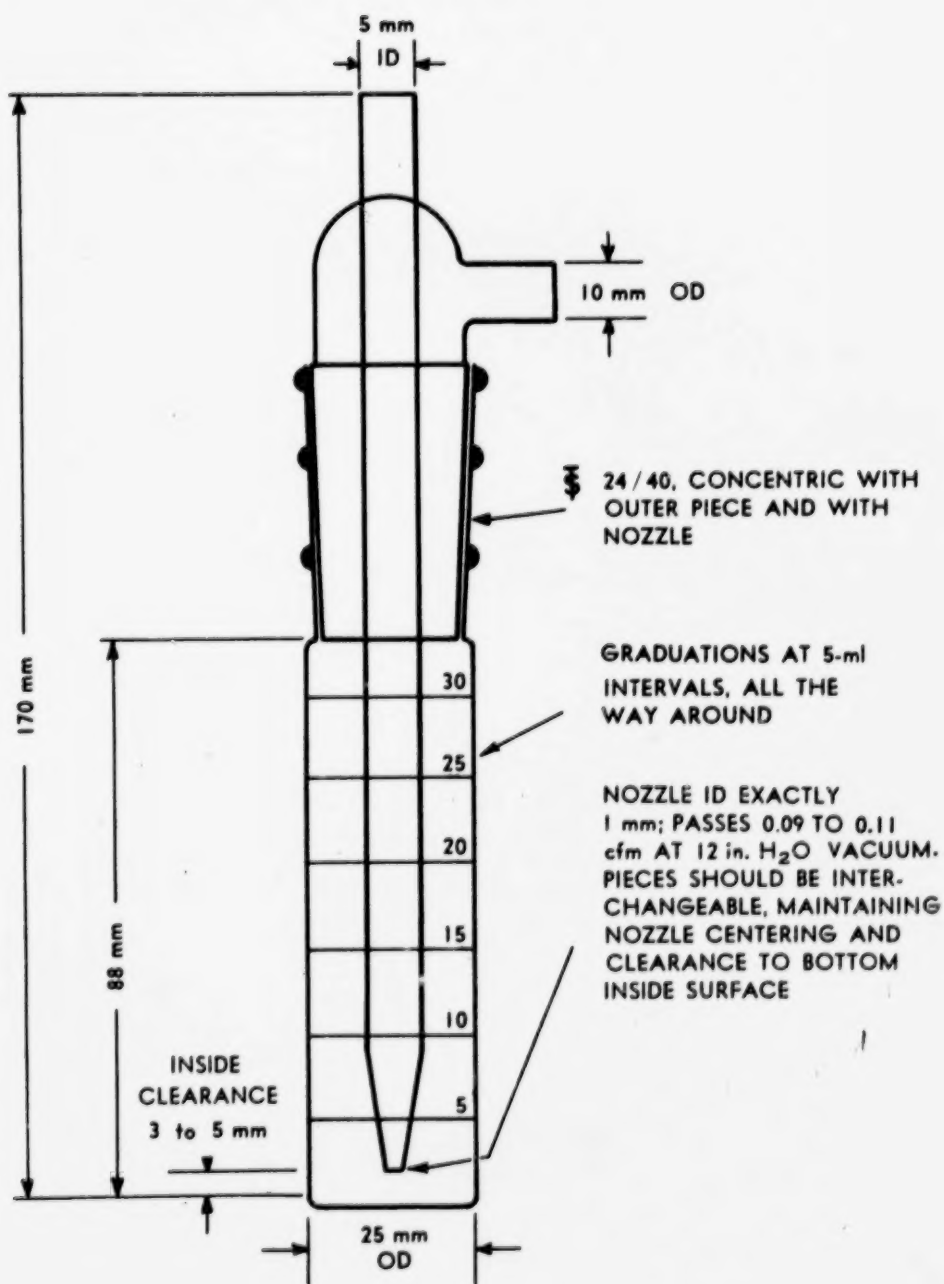


FIGURE 3. ALL-GLASS MIDGET IMPINGER (THIS IS A COMMERCIALY STOCKED ITEM).

Samples may be aliquoted either before or after acidification if very large concentrations of oxidant are expected. In the former case, dilute the aliquot to 10 ml with unexposed absorbing reagent and proceed in the usual manner. In the latter case, dilute the aliquot to volume with reagent blank mixture. Aliquoting after acidification is not as reliable and should be used only to save a sample when unexpectedly large concentrations of oxidant are encountered. The calculations should include the aliquoting factor.

Standardization. Add the freshly prepared, dilute, standard iodate solution in graduated amounts of 0.10 to 0.45 ml (measured accurately in a graduated pipet or small buret) to a series of 25-ml, glass-stoppered, graduated cylinders. Add sufficient alkaline potassium iodide solution to make the total volume of each exactly 10 ml. Acidify and determine the absorbance of each standard as with the samples.

Calculations. For convenience, standard conditions are taken as 760 mm of mercury and 25°C; thus, usually only slight correction by means of the well-known perfect gas equation is required to get V, defined as the standard volume of the air sampled in liters. Ordinarily this correction may be omitted. Quantities, customarily expressed in terms of ozone, may be expressed as microliters, defined as V times ppm ozone. It has been determined empirically that 1 mole of ozone liberates 0.65 mole of iodine (I₂) by this procedure. The strength of the stock standard potassium iodate solution is computed on the basis of I₂ ⇌ 1/3 KIO₃, and the following:

Standard molar volume (25°C, 760 mm) = 24.47 liters;

molecular weight KIO₃ = 214.02; 1 ml stock solution = 400 μl

$$(\text{O}_3) = \frac{400 \times 10^{-6}}{24.47} \times \frac{0.65}{3} \times 214.02 = 0.758 \times 10^{-3} \text{ g KIO}_3$$

Plot the absorbances of the standards (corrected for the blank) against milliliters of dilute standard iodate solution. Beer's Law is followed. Draw the straight line giving the best fit and determine the value in milliliters of the diluted potassium iodate solution intercepted at an absorbance of exactly 1. This value multiplied by 40 gives the standardization factor M, defined as the number of microliters of ozone required by 10 ml of absorbing reagent to give a final absorbance of 1. For 2-cm cells this value is 9.13. Then:

$$\text{ppm oxidant (expressed as O}_3\text{)} = \text{corrected absorbance} \times \frac{M}{V} \quad (1)$$

If the volume of the air sample, V, is a simple multiple of M, calculations are simplified. Thus, for the M value of 9.13 previously cited, if exactly 9.13 liters of air is sampled through the impinger, the corrected absorbance is also ppm directly. If other volumes of absorbing reagent are used, V is taken as the volume of air sample per 10 ml of absorbing reagent.

DISCUSSION OF PROCEDURE

Sampling efficiency. When two impingers are placed in series, iodine will very rarely be liberated from the solution in the second absorber. Thus, the sampling efficiency is very high. Fritted bubblers, which also appear to have equally high sampling efficiencies, usually give, however, less iodine for a given amount of ozone and should not, therefore, be used. (This is due to the complex chemistry of ozone in alkaline iodide solution. It appears that hypoiodite is the primary product, but that some is lost through side reactions, with resulting variation in the stoichiometry.² Potassium iodate is a convenient chemical to use for standardization, although iodate is probably not produced by absorption of ozone.)

Stability of exposed absorbing reagent. Studies have indicated that most of the losses in exposed reagent occur in the first day. The reagent may then be stored for as long as a week or more with little further change. Use of analytical-grade reagents and of carefully cleaned glassware reduces losses.

Acidification step. Certain irreversible losses of microquantities of iodine occur during the acidification of alkaline iodide solution. This is probably the explanation for the relationship of 0.65 mole of iodine liberated for each mole of ozone absorbed. Very slow acidification will yield less iodine. The most reproducible procedure is to add the acid rapidly with vigorous stirring.

Interferences. The negative interferences from reducing gases such as sulfur dioxide and hydrogen sulfide are very serious (probably on a mole-to-mole equivalency). The procedure is very sensitive to reducing dusts that may be present in the air or on the glassware. Losses of iodine also occur even on clean glass surfaces, and thus the manipulations should minimize this exposure.

Elimination of the interference of sulfur dioxide, even when it was present in as high as hundredfold ratio to oxidant, has been accomplished recently³ by incorporating an extra large (140-ml) absorbing U-tube in the sampling train upstream from the impinger. The absorbent, which removes sulfur dioxide without loss of oxidant, is glass fiber paper impregnated with chromium trioxide. (Drop 15 ml of aqueous solution containing 2.5 g chromium trioxide and 0.7 ml concentrated sulfuric acid uniformly over 60 in.² of paper, and dry in an oven at 80 to 90°C for 1 hour. Cut the paper into 1/4- x 1/2-in. strips, each folded once into a V-shape, pack into the U-tube, and condition by drawing air through tube overnight.) The absorbent has a long life (at least 1 month). If it becomes visibly wet from sampling humid air, it must be dried (with dry air) before further use.

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Determination of Aliphatic Aldehydes: 3-Methyl-2-benzothiazolone Hydrazone Hydrochloride (MBTH) Method*

INTRODUCTION

The MBTH method is applicable to the determination of total water-soluble aliphatic aldehydes (measured as formaldehyde) in ambient air. The results of limited field testing show that as little as 2 ppb aldehydes in air can be determined when air is sampled at a rate of 0.5 liter per minute over a 24-hour period.

Aliphatic aldehydes react with MBTH in the presence of ferric chloride to form a blue cationic dye in acidic media.¹ The aldehydes in ambient air are collected in a 0.05 percent aqueous MBTH solution. The resulting azine is then oxidized by a ferric chloride-sulfamic acid solution to form the blue dye, which can be measured at 628 mμ.²

REAGENTS

The various reagents are prepared on a weight-volume basis (i. e., grams per 100 ml of solution).

Collecting reagent. The collecting reagent is a 0.05 % aqueous 3-methyl-2-benzothiazolone hydrazone hydrochloride (MBTH) solution. This colorless solution is filtered by gravity if slightly turbid and is stable for at least 1 week, after which it becomes pale yellow. Stability may be increased by storing in a dark bottle in the cold. MBTH can be either synthesized¹ or purchased (Aldrich or Eastman).

Oxidizing reagent. An aqueous solution containing 1.6 % sulfamic acid and 1.0 % ferric chloride is used. Both reagents should be ACS reagent grade.

Dimedon. Dimedon (5,5-dimethylcyclohexanedione-1,3) is used for the standardization of formaldehyde. Prepare 500 ml of an aqueous solution containing 1.07 g of dimedon.

Formaldehyde solution. Accurately dilute 2.7 ml of commercially available 37 to 39 % aqueous ACS reagent grade formaldehyde to a liter with distilled water. This solution will contain approximately 1 g of formaldehyde per liter. Standardize this solution by the following procedure.³

Place 50 ml of the dimedon reagent in each of three clean, dry, glass-stoppered Erlenmeyer flasks and add to each 10 ml of the formaldehyde stock solution. Shake the mixtures, let stand overnight (over a weekend if possible), and filter through previously weighed sintered-glass (or other filtering) crucibles. Dry the precipitates

*Prepared by Thomas R. Hauser, Field Studies Branch, Division of Air Pollution, Public Health Service. Approved by the Interbranch Chemical Advisory Committee, May 1964.

in vacuum over phosphorus pentoxide to constant weight. The gravimetric factor for converting the weight of precipitate to weight of formaldehyde is 0.1027. The grams of CH_2O per ml of 37 to 39% solution equals, therefore,

$$\frac{\text{weight of precipitate} \times 0.1027 \times 100}{2.7}$$

EQUIPMENT

Spectrophotometer or colorimeter. Any instrument capable of measuring absorbance between 600 and 700 $\text{m}\mu$ is acceptable for quantitative analysis.

Absorber. Any absorber containing a fritted bubbler of 40- to 80- μ porosity (Corning coarse frit) and having a capacity of at least 75 ml is acceptable. The absorber used in developing the procedure was a 100-ml polypropylene test tube.

Air-metering and flow control devices. Any devices capable of measuring and regulating airflows with an accuracy of ± 2 percent are acceptable.

Air pump. Any pump capable of pulling air through the sampling assembly at a rate of 0.5 liter per minute for 24 hours is acceptable.

ANALYTICAL PROCEDURE

Sampling and analysis. Assemble a sampling train in the following order: Absorber, trap to protect the flow device, flow-metering device, flow control device, and air pump. (The flow control and flow-metering devices may be one piece of equipment such as a precalibrated limiting orifice.) After 35 ml of the collecting reagent is added in the absorber, air is drawn through the system at a rate of approximately 0.5 liter per minute for 24 hours. When sampling is completed, adjust the volume of the collecting reagent back to the original 35 ml with distilled water and allow to stand for 1 hour. This insures complete reaction of the aliphatic aldehydes with the MBTH. Pipette 10 ml of the sample into a test tube, add 2 ml of the oxidizing reagent, and mix thoroughly. After it has stood for 12 minutes, the absorbance is measured at 628 $\text{m}\mu$ against an appropriate blank prepared from nonaerated laboratory reagents. The amount of aliphatic aldehydes (reported as formaldehyde) per milliliter test solution is readily ascertained from the absorbance-concentration curve. Since the volume of air sampled had been measured, the concentration of aldehydes in the air can be readily calculated from the following equation:

$$\text{ppm (total aldehyde as } \text{CH}_2\text{O)} = 0.814 \frac{VC}{FT} \quad (1)$$

where V = total volume of collecting reagent = 35 ml

C = μg aldehyde found (as CH_2O) per ml collecting reagent

F = airflow-sampling rate in liters per minute

T = total sampling time in minutes

0.814 = total μl that one μg CH_2O will occupy at 25°C and 760 mm

Standardization. For spectrophotometers having an absorbance range of 0.0 to 1.0, five test solutions ranging from 0.1 to 0.7 μg of formaldehyde per ml of 0.05% MBTH are prepared. After it has stood for 1 hour, 10 ml of each test solution is placed in a test tube, and 2 ml of the oxidizing reagent added. After mixing, allow the tube to stand for at least 12 minutes for complete color development. The absorbance is then determined on the spectrophotometer at 628 $m\mu$ against an appropriate blank; the blank is light yellow. Plot absorbance versus μg of formaldehyde per ml of test solution to obtain the calibration curve.

Discussion. The average collection efficiency of formaldehyde in air has been determined to be 84% when air was sampled at a rate of 0.5 liter per minute over a 24-hour period in 35 ml of collecting reagent. Collection efficiency data are not available for higher or lower sampling rates, longer or shorter sampling periods, and larger or smaller volumes of collecting reagent. The collection efficiency as well as the sensitivity of the method may be increased or decreased depending upon the conditions selected for sampling. When sampling conditions other than those described in the procedure are employed, the collection efficiency for the new conditions should be determined.

The blank solution for colorimetric analysis may be prepared from nonaerated laboratory reagents. During the initial determination of collection efficiency, six bubblers were placed in series. In no case was any formaldehyde detected past the first bubbler, and no significant differences were observed in blanks prepared from the contents of the second bubbler or from nonaerated laboratory reagents. During repeated determinations, the contents of the first bubbler showed no difference in formaldehyde content when compared with blanks prepared from either the contents of the second bubbler or from laboratory reagents. Consequently, it is unnecessary to have a second bubbler connected in series in the sampling train.

The molar absorptivity observed for formaldehyde at the wavelength maxima of 628 $m\mu$ is 50,000. The Beer's Law study exhibited a linear relationship for formaldehyde concentrations of 0.0 to 1.72 μg per ml of test solution over an absorbance range of 0.0 to 2.35 when 1.0-cm cells were employed. The study also demonstrated excellent reproducibility in absorbance when duplicate samples were analyzed, and little, if any, deviation from the standard curve was observed over the entire concentration range reported above.

In the procedure, the addition of the oxidizing reagent to 0.05% MBTH test solutions containing formaldehyde gives optimum color conditions when the concentrations of ferric chloride and sulfamic acid in the oxidizing reagent are 1.0 and 1.6% respectively. Full color development is observed after 10 minutes oxidation time and the color is stable for at least an additional hour. Increasing the concentration of the sulfamic acid in the oxidizing reagent lowers the absorbance and lengthens the oxidation period; with a lesser concentration, a persistent turbidity is always observed. Increasing the ferric chloride content in the oxidizing reagent produces a more colored blank whereas a decrease results in decreased absorbance.

When the concentration of the MBTH is increased to more than 0.05% the solutions become turbid. Smaller concentrations of MBTH result in a loss of color intensity. A 15% decrease in absorbance is observed when the concentration of the MBTH is reduced from 0.05 to 0.02%, even though the solutions are free of turbidity. The concentration of the MBTH must be in excess of that of the aliphatic aldehydes collected. If 60.4 μ g of formaldehyde is absorbed in the 35 ml of collecting solution, an optical density of 2.35 is obtained. This amount of formaldehyde requires 870 μ g of MBTH for complete reaction. There is 17,500 μ g of MBTH in 35 ml of collecting solution, representing a 20-fold excess. If formaldehyde becomes present in excess, only a negligible concentration of MBTH is available to react with the azine, and the final color intensity is very weak. This point may become very important in the analysis of an air sample.

The time study of the reaction of microgram quantities of formaldehyde with 0.05% MBTH shows that the reaction is complete in approximately 45 minutes; therefore, a reaction time of 1 hour is selected for this procedure. Formaldehyde is fairly stable in 0.05% MBTH since only approximately 5% of the formaldehyde is lost after standing in the MBTH for 13 days. The samples are, therefore, stable enough for later analysis.

INTERFERENCES

The following classes of compounds react with MBTH to produce colored products. These are aromatic amines, imino heterocyclics, carbazoles, azo dyes, stilbenes, Schiff bases, the aliphatic aldehyde 2,4-dinitrophenylhydrazones, and compounds containing the p-hydroxy styryl group. Most of these compounds are not gaseous or water soluble and consequently should not interfere with the analysis of water-soluble aliphatic aldehydes in the atmosphere.

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Determination of Acrolein: 4-Hexylresorcinol Method *

INTRODUCTION

This method¹ is designed for the determination of acrolein in the atmosphere over the range of about 20 ppb to at least 10 ppm. A blue-purple color is formed by the reaction of acrolein with 4-hexylresorcinol in the presence of trichloroacetic acid and mercuric chloride. Owing to its greater sensitivity and specificity, its use is recommended over that of other available methods. This procedure has been used satisfactorily in the laboratory but has been field tested to only a limited extent.²

REAGENTS

All reagents are analytical grade. Precautions should be taken in handling most of these solutions since they are corrosive to the skin or poisonous.

Ethanol (96%).

Trichloroacetic acid solution, saturated. It is well to prepare large quantities of this solution at one time to be sure of uniformity. It is recommended that the entire contents of the reagent bottle be dissolved at one time by adding 10 ml of water for each 100 g of the solid acid and heating on a water bath. (The resulting volume of solution is about 70 ml per 100 g of solid acid.) Every new batch of the solution should be standardized with acrolein. CAUTION: Both the solid acid and solution are corrosive to the skin. Breathing of the fumes evolved during preparation of the solution should be avoided.

Mercuric chloride solution. Three g of HgCl_2 is dissolved in 100 ml of ethanol.

4-Hexylresorcinol solution. Five g of this material (mp 68 to 70°C) is dissolved in 5.5 ml of 96% ethanol. (This yields about 10 ml of solution.)

Mixed reagent. Mix, in order, reagents in the following proportions: 5 ml ethanol, 0.1 ml of 4-hexylresorcinol solution, 0.2 ml mercuric chloride solution, and 5 ml saturated trichloroacetic acid solution. The mixed reagent may be stored for a day at room temperature. Prepare the needed quantity by selecting an appropriate multiple of these amounts. Protect from direct sunlight.

Acrolein, purified. Freshly prepare a small quantity (less than 1 ml is sufficient) by distilling 10 ml of the purest grade of acrolein commercially available. (The latter material should be stored in a refrigerator to retard polymerization.) The distillation should be done in a hood because the vapors are irritating to the eyes. Reject the first 2 ml of distillate.

*Prepared by Israel R. Cohen and Bernard E. Saltzman, Laboratory of Engineering and Physical Sciences, Division of Air Pollution, Public Health Service. Approved by Interbranch Chemical Advisory Committee. May 1964.



Water bath. Any type of container in which the temperature can be maintained at 58 to 60°C is acceptable.

Air pump. A suction pump capable of drawing the gas to be sampled through the assembly at the rate of up to 2 liters per minute for intervals of up to 1 hour is acceptable. There should be a trap at the inlet to protect the pump from the corrosive reagent.

Air-metering device. A glass rotameter or other device capable of measuring flows of up to 2 liters per minute with an accuracy of $\pm 2\%$ is recommended.

Spectrophotometer or colorimeter. This device should be capable of measuring the developed color at 605 m μ . The absorption band is rather narrow, and thus a lower absorptivity may be expected in a broad-band instrument.

ANALYTICAL PROCEDURE

Direct procedure (preferred). The gas is drawn for 30 minutes at 2 liters per minute or for 60 minutes at 1 liter per minute through a train of two bubblers, each containing exactly 10 ml of mixed reagent. An extra bubbler containing water may be added as a trap to protect the pump. Note the total volume of the air sample. If the sample air temperature and pressure deviate greatly from 25°C and 760 mm Hg, measure and record these values. If appreciable evaporation has occurred, add ethanol to restore the volume to its original graduation mark. (Excessive evaporation or possible decomposition may occur if sampling is conducted for longer than 1 hour, or is done of more than 60 liters of air. This volume will suffice to determine as little as 20 ppb acrolein.)

The sample solutions are then immersed in the 60°C bath for 15 minutes to develop the colors. The test tubes are cooled in running water immediately upon removal from the bath, and the absorbances are read at 605 m μ about 15 minutes later. This time may be prolonged for up to 2 hours with no appreciable loss in accuracy. Alternatively, if no bath is available, the sample solutions may be stored for 2 hours at room temperature for color development. The absorbances are usually determined in a 1-cm cell. For very small acrolein concentrations it may be convenient to use a cell with a longer path length.

A portion of mixed reagent is taken as a blank and treated in the same manner as the sample solutions.

Alternative procedure for delayed determination. When it is inconvenient to read the colors immediately after sampling, 96% ethanol instead of mixed reagent may be used as a collecting reagent. The bubblers, each containing 10 ml of ethanol, are cooled in ice water during the sampling period; the sampling procedure is otherwise the same as above. Do not sample more than 10 liters of air. The concentration of acrolein sampled should be at least 0.1 ppm (for which 5-cm cells are needed for accurate reading of the developed color). The collected sample may be stored for as long as a week at ice temperature.

The determination is completed by mixing exactly 5 ml of the ethanolic sample solution (or a smaller portion diluted with ethanol to 5 ml) with the other ingredients in the same proportions as in the mixed reagent. The colors are then developed and read as described above in the direct procedure. The absorptivity obtained is 70% of that by the direct method.

Standardization. Prepare a series of test tubes containing 0, 1, 2, 3, and 4 ml of dilute standard acrolein solution (8.4 $\mu\text{g/ml}$), respectively; add to each sufficient ethanol to make exactly 5 ml. To each tube, add, in order, exactly 0.1 ml 4-hexylresorcinol solution, 0.2 ml mercuric chloride solution, and 5 ml trichloroacetic acid solution. Mix, develop, and read the colors as described in the direct procedure. Plot the absorbances against the micrograms of acrolein and determine the slope of the line obtained.

A more accurate, though less convenient, standardization of the direct procedure is obtained by sampling acrolein-air mixtures from a mylar bag (about 3 ft²) directly into the mixed reagent. These mixtures are prepared by injecting measured volumes of the strong acrolein standard solution with a syringe (conveniently of 250- μl capacity) through a serum bottle cap on a T connection into the airstream as the bag is filled. Total air volume is computed from the measured flow rate and filling time.

Calculations.

$$\text{ppm acrolein} = \frac{A \times b}{a \times 2.29 \times V} \quad (1)$$

A = absorbance of the reacted sample solution

a = absorbance of standards per μg of acrolein
(slope of the standard plot)

2.29 = weight in μg of 1 μl of gaseous acrolein at
25°C, 760 mm Hg

V = liters of air sample, corrected to 25°C, 760 mm
Hg by means of the perfect gas equation (this
correction may ordinarily be omitted)

b = aliquoting and correction factor. There are
three mathematical cases:

The factor is 1.00 for the direct procedure
standardized with gas mixture.

For the direct procedure standardized with
liquids, allowance must be made for the fact
that the standardization yields only 70% of the
absorptivity of gas samples, and final volumes
are 10.3 ml rather than 10.0 ml. The factor
is, therefore, 0.68:

$$0.70 \times \frac{10.0}{10.3} = 0.68$$

For the alternative procedure, a half aliquot is taken in the procedure as described. Moreover, it is desirable to correct for incomplete absorption of sample. If the estimated collection efficiency of the total train is e , the factor is $2.0/e$.

The factors $b/a \times 2.29$ are conveniently combined into a single standardization constant.

Add the ppm values computed for the contents of each bubbler in the sampling train to get the total present in the sample.

DISCUSSION OF PROCEDURE

Absorption efficiency. The collection efficiency, when mixed reagent is used for sampling, is 70 to 80% in the first bubbler and 95% in the first two bubblers, even with a 40- to 50-liter sample. (It appears likely that use of an absorber with a finer frit, similar to that shown in Figure 1 or Figure 5, would raise these efficiencies.

The collection efficiency is lower when ethanol is used as the absorbing reagent, since the volatile acrolein is not fixed by chemical reaction but is merely in solution. Satisfactory collection efficiency (80 to 90%) can be obtained with two bubblers in series at ice temperature if sample volumes are limited to less than 10 liters. Use of a dry ice-acetone bath permits sampling of greater air volumes at smaller concentrations.

Applicability of Beer's Law. The absorbances at 605 m μ are linear for at least 1 to 30 μg of acrolein in the 10-ml portions of mixed reagent. The absorptivities of the colored product for the direct and alternative methods are 0.50 and 0.35 $\mu\text{g}^{-1} \text{ ml cm}^{-1}$ respectively. With the alternative method, for example, using a cell with a 1-cm path length, the standard color containing 1 ml of dilute standard solution (which thus contains 8.4 μg of acrolein in 10.3 ml total volume) should have an absorbance of $0.35 \times 8.4/10.3 = 0.29$.

Interferences. There is no interference from ordinary quantities of sulfur dioxide, nitrogen dioxide, ozone, and most organic air pollutants. A slight interference occurs from dienes: 1.5% for 1,3-butadiene, and 2% for 1,3-pentadiene. The red color produced by some other aldehydes and undetermined materials does not interfere in the spectrophotometric measurement.

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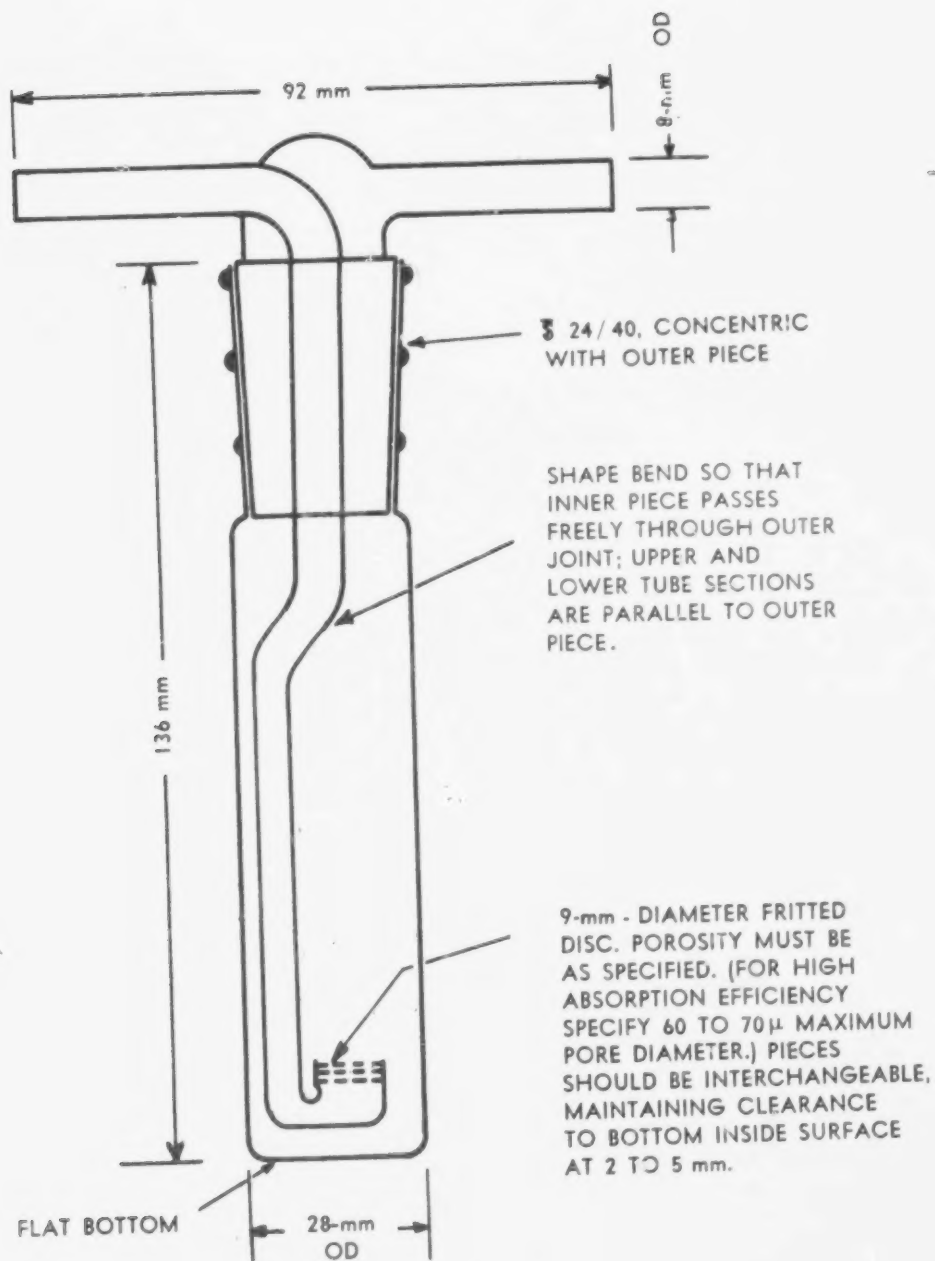


FIGURE 5. ALL-GLASS MIDGET BUBBLER WITH FRITTED-DISC INLET.

Determination of Formaldehyde: Chromotropic Acid Method*

INTRODUCTION

Formaldehyde in the ambient air can be determined by using the chromotropic acid method in the concentration range of about 0.01 to at least 200 ppm.¹ To measure 0.01 ppm of formaldehyde it is necessary to sample about 60 liters of air. A purple monocationic chromogen is formed when formaldehyde reacts with a chromotropic acid-sulfuric acid solution. Compounds such as formic acid, dextrose, methanol, and others, which decompose under the test conditions to yield formaldehyde, will also be measured by this method. It has been used extensively to measure formaldehyde in synthetic atmospheres and has been used satisfactorily to measure formaldehyde in city atmospheres.^{2,3}

REAGENTS

Chromotropic acid, 4,5-dihydroxy-2,7-naphthalenedisulfonic acid. The chromotropic acid presently commercially available is practical grade; be certain, therefore, to recheck the calibration curve with each new supply.

Sampling solution, 0.1% chromotropic acid in concentrated sulfuric acid. Dissolve 1.0 g of chromotropic acid in concentrated sulfuric acid and dilute to 1 liter. (DANGER: keep off skin and eyes.) The solution is stable for at least 1 month when stored in bottles protected from light.

Iodine, 0.1 normal (approximate). Dissolve 25 g of potassium iodide in about 25 ml of water, add 12.7 g of iodine and dilute to 1 liter.

Iodine, 0.01 normal. Take a 100-ml portion of the 0.1 normal iodine solution and dilute to 1 liter. Standardize against sodium thiosulfate or arsenious oxide.

Starch solution, 1%. Make a paste of 1 g of soluble starch and 2 ml of water, and slowly add the paste to 100 ml of boiling water. Cool and store in a stoppered bottle.

Buffer solution. Dissolve 80 g of anhydrous sodium carbonate in about 500 ml of water. Add 20 ml of glacial acetic acid and dilute to 1 liter. The pH is adjusted to 9.6 (± 0.1) by using acetic acid or sodium carbonate.

Sodium bisulfite, 1%. Dissolve 1 g of NaHSO_3 in 100 ml of water.

Stock formaldehyde solution. Prepare a solution containing approximately 1 g of formaldehyde per liter of solution by pipetting 3 ml of 37 to 39% reagent grade formaldehyde into a 1-liter volumetric flask and diluting to the mark with distilled water. Standardize this stock solution as described below in the standardization section.

*Prepared by Stanley E. Sleva, Air Pollution Training, Training Program, Public Health Service. Approved by Interbranch Chemical Advisory Committee. July 1964.

Dilute standard formaldehyde solution. One hundred ml of this stock formaldehyde solution is diluted to 1 liter with distilled water before it is needed for preparation of the calibration curve. The formaldehyde concentration of this diluted solution is about 100 g/ml.

APPARATUS

Samplers. An all-glass absorber, similar in design to that shown in Figure 1, with nozzle or fritted-tube inlet is recommended. If a fritted tube is used, a frit with maximum pore diameter of about $10\ \mu$, equivalent to Corning EC or Ace Glass A, is recommended.

Air pump. A pump capable of pulling at least 2 liters of air per minute for 60 minutes through the sampling train is required.

Air-metering and flow control devices. Devices capable of measuring and controlling airflows with an accuracy of $\pm 2\%$ are needed. The flow meter calibration should provide for temperature and pressure corrections.

Thermometer (or other temperature-measuring device.) This device should have an accuracy of $\pm 2^\circ\text{C}$.

Mercury manometer (or other vacuum-measuring device.) This device should have an accuracy of $\pm 5\ \text{mm Hg}$.

Spectrophotometer or colorimeter. This device should be capable of measuring color intensity at 580 $m\mu$.

ANALYTICAL PROCEDURE

Assemble the sampling train in the following order: Bubbler, manometer, flow-metering device, trap to protect pump, flow control device, and pump. Measure 10 ml of sampling solution into each bubbler. Draw the air to be sampled through the sampling train at a rate of up to 2 liters per minute. After sampling, transfer resulting solution to a pyrex test tube.

Analysis. Heat is necessary to obtain full color development. This may be accomplished by actually heating the sample solutions in a 50°C bath for 15 minutes or by the heat of reaction resulting from the addition of 1 ml of water to each 10 ml of sample solution. The development procedure decided upon should also be used in preparing the standard calibration curve. After full color development, transfer the sample solutions to about 25°C , transfer to proper cells, and measure the absorbance against a blank at 580 $m\mu$. The blank solution is 10 ml of 0.1% chromotropic acid solution, treated in the same manner as the air-sampled solution.

STANDARDIZATION

Standardization of stock formaldehyde solution. Pipet 1 ml of stock formaldehyde solution into one flask and 1 ml of water into another flask. Add 25 ml of 1% sodium bisulfite and 1 ml of 1% starch solution into each flask. Titrate these solutions with 0.1 normal iodine to a dark blue color. Destroy the excess iodine by adding a few drops of 0.05 normal sodium thiosulfate, then return to a faint yellow color by carefully adding 0.01 normal iodine.

SELECTED METHODS

Chill the flasks in an ice bath and add 25 ml of chilled sodium carbonate buffer to each flask. Place the flasks in an ice bath for an additional 10 minutes and then titrate the liberated sulfite to the faint blue color with 0.01 normal iodine. The volume of 0.01 normal iodine solution used in the blank titration is subtracted from the sample titration. Since 1 ml of 0.01 normal iodine solution is equivalent to 0.15 mg of formaldehyde, the concentration of the standard formaldehyde solution in μg per ml can be determined by the equation:

$$\mu\text{g of formaldehyde/ml} = V_{I_2} \times N_{I_2} \times 1.5 \times 10^4 \quad (1)$$

V_{I_2} = ml of 0.01 normal iodine solution used to titrate the liberated sulfite corrected for blank titration

N_{I_2} = exact normality of the 0.01 normal iodine solution.

Preparation of calibration curve. Transfer separately exactly 20, 15, 10, 5, and 2.5 ml of the dilute standard formaldehyde solution to five 100-ml volumetric flasks and dilute each to the mark with distilled water. These five test solutions should contain approximately 20, 15, 10, 5, and 2.5 μg , respectively, of formaldehyde per ml of test solution. Pipet 1 ml of each test solution into separate 10-ml volumetric flasks. Add to each volumetric flask about 7 ml of 0.1% chromotropic acid solution (CAUTION: heat of reaction) and cool to room temperature; then dilute to the mark with additional 0.1% chromotropic acid solution. The heat of reaction resulting from the addition of the chromotropic acid to 1 ml of aqueous formaldehyde solution is usually sufficient to develop the purple color fully. The additional treatment of transferring the contents of the volumetric flasks to pyrex test tubes and then heating at 100°C for 15 minutes will guarantee full color development. Allow the solutions to cool to about 25°C and then measure the absorbance of each test solution against a blank at $580\text{ m}\mu$. The blank solution consists of 1 ml of distilled water treated in the same manner as the test solution. The formaldehyde concentration in the final color-developed solution is approximately 2, 1.5, 1, 0.5, and 0.25 $\mu\text{g/ml}$. Prepare a calibration curve by plotting absorbance versus the formaldehyde concentration in $\mu\text{g/ml}$ of the final color-developed solution.

Calculations. Correct the volume of air sampled to the volume at standard conditions of 25°C and 760 mm Hg:

$$V_s = V \times \frac{(P - P_m)}{760} \times \frac{298}{(t + 273)} \quad (1)$$

V_s = volume of air in liters at standard conditions

V = volume of air in liters as measured at sampling conditions

P = barometric pressure in mm of mercury

P_m = suction at meter in mm of mercury

t = temperature of the sampled air, $^\circ\text{C}$

The concentration of formaldehyde in the sampled atmosphere may be calculated by using the following equations:

$$\text{ppm (vol)} = \frac{C \times B}{1.23 V_s} \quad (2)$$

$$\mu\text{g of formaldehyde/m}^3 = \frac{C \times B \times 1000}{V_s} \quad (3)$$

Where

m^3 is cubic meters of air

C is the concentration of formaldehyde in $\mu\text{g/ml}$ of the final color-developed solution obtained from calibration curve

B is the total ml of sampling solution

V_s is the volume of sampled air in liters at standard conditions of 25°C and 760 mm Hg

1.23 is the vapor density of formaldehyde in $\mu\text{g}/\mu\text{l}$ calculated at 25°C and 760 mm Hg

DISCUSSION OF PROCEDURE

Sampling efficiency. The use of sampling collectors with fritted stems and flow rates up to 1 liter per minute give collection efficiencies of at least 95% with a single sampler.

Stability of colored reaction product and sampling solution. An increase in absorbance of the reaction product of about 3% is obtained after it has stood for 1 day, and about 10%, after 8 days.

The chromotropic acid sampling solution can be kept for at least 2 months if the solution is kept in bottles protected from light. It is important to protect the sampling solution from sunlight during the actual sampling period. On a bright day, the solution tends to become straw or light tan in color if unprotected. Wrapping the sampling apparatus with aluminum foil is a convenient method of eliminating this problem.

Interferences. The chromotropic acid procedure has very little interference from other aldehydes. Saturated aldehydes give less than 0.01% positive interference, and the unsaturated aldehyde acrolein results in a few percent positive interference. Ethanol and higher molecular weight alcohols and olefins in mixtures with formaldehyde are negative interferences,¹ but concentrations of alcohols in air are usually much smaller than formaldehyde concentrations, which creates no grave problems.

Phenols result in a 10 to 20% negative interference when present at an 8 to 1 excess over formaldehyde. They are, however, ordinarily present in the atmosphere at lesser concentrations than formaldehyde, which creates no significant problem.

Ethylene and propylene in a 10 to 1 excess over formaldehyde resulted in a 5 to 10 % negative interference, and 2-methyl-1, 3-butadiene in a 15 to 1 excess over formaldehyde showed a 15% negative interference. Aromatic hydrocarbons also constitute a negative interference.

Interferences of olefins and aromatic hydrocarbons can be substantially reduced by using an aqueous sodium bisulfite solution as a collecting medium in place of the chromotropic sulfuric acid sampling solution and making minor modifications in the procedure. This aqueous solution has a lower collection efficiency for these interfering substances.

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Determination of Sulfate in Atmospheric Suspended Particulates: Turbidimetric Barium Sulfate Method *

INTRODUCTION

Suspended particulate matter is collected over a 24-hour period on an 8- by 10-inch glass fiber filter by using a high-volume sampler. A water extract of the sample is treated with barium chloride to form barium sulfate. The turbidity caused by the barium sulfate is a measure of the sulfate content. Aliquoting is adjusted so that samples containing 1 to 20 $\mu\text{g}/\text{m}^3$ (the expected range of atmospheric samples) can be measured. The sensitivity of the turbidimetric analytical procedure is 50 μg of sulfate. Nephelometrically, as little as 2 μg of sulfate can be measured.

REAGENTS

All reagents are made from analytical-grade chemicals.

Hydrochloric acid (10 normal). Dilute 80 ml of concentrated reagent grade hydrochloric acid to 100 ml with distilled water.

Glycerol-alcohol solution. Mix 1 volume of glycerol with 2 volumes of absolute ethyl alcohol (reagent grade).

Barium chloride. Use 20- to 30-mesh crystals.

Standard sulfate solution (100 $\mu\text{g SO}_4^{2-}$ per ml). Dissolve 0.148 g of anhydrous sodium sulfate (dry if necessary) in distilled water and dilute to 1 liter.

EQUIPMENT

High-volume sampler. A motor blower filtration system with a sampling head, which can accommodate an 8- by 10-inch glass fiber filter web and is capable of an initial flow rate of about 60 ft^3 per minute, is used and is shown in Figure 6. These samplers are available from General Metals Works, Box 30, Bridgetown Road, Cleves, Ohio; and Staplex Company, 774 Fifth Avenue, Brooklyn 32, N. Y., among others.

Glass fiber filters. Use 8- by 10-inch size, Mine Safety Appliances Company, 1106 BH or any comparable make.²

Refluxing apparatus. Use 125-ml flask fitted with reflux condenser and hot plate.

Funnels and Whatman No. 1 filter paper.

Cuvettes. Use cuvettes with a 1-inch light path and plastic stoppers.

* As used by the National Air Sampling Network.

Prepared by Norman A. Huey, Laboratory of Engineering and Physical Sciences, Division of Air Pollution, Public Health Service. Approved by the Interbranch Chemical Advisory Committee, July 1964.

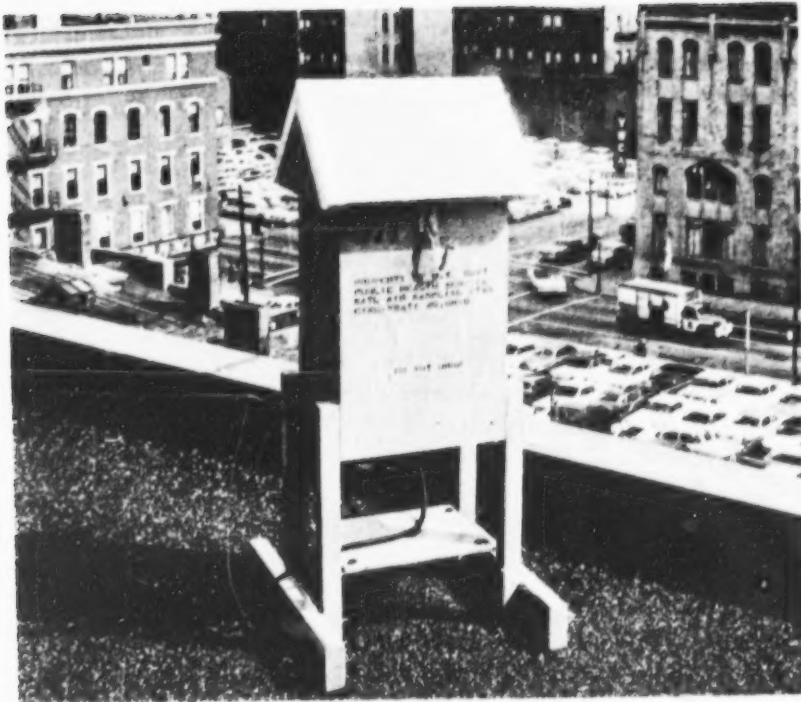


FIGURE 6. TYPICAL SAMPLER ASSEMBLY (ABOVE) AND HIGH-VOLUME AIR SAMPLER (BELOW).

Pipettes. Use 20-, 4-, and 1-ml pipettes.

Spectrophotometer or colorimeter. This device should be suitable for measurement at 500 m μ .

PROCEDURE

Sampling. Using the Hi-Vol sampler, collect the particulates from approximately 2,000 m³ of air. Twenty-four hours is the usual sampling period. The air volume is calculated from the sampling time and the average of airflow measurements taken at the start and end of the sampling period.

Sample preparation. The sample filter is folded upon itself along the 10-inch axis to facilitate storage and transportation. This fold may result in a nonhomogeneous area in the sample. All sample aliquoting is, therefore, made across the fold. Using a wallpaper cutter or other suitable device and a straight edge, cut a 3/4- by 8- inch strip from the filter. Place this in the refluxing apparatus with 25 ml of distilled water and reflux for 90 minutes. Filter through Whatman No. 1 paper, rinsing with distilled water till 50 ml of filtrate is obtained.

Analytical procedure. Place a 20-ml portion of the prepared sample into a clean, dry, 1-inch cuvette. Add 1 ml of 10 N HCl, 4 ml of the glycerol-alcohol solution, and mix. Determine the absorbance at 500 m μ against a reference cuvette containing distilled water. This reading is subtracted from the final reading. It corrects for unmatched cuvettes and other impurities in the sample. Add approximately 0.25 g of barium chloride crystals and shake until dissolved. Let stand for 40 minutes at room temperature (20 to 30°C). Measure the absorbance at 500 m μ against the reference cuvette containing distilled water.

A standard sulfate solution should be analyzed with each batch of samples. Deviations up to 5% from the standard curve can be expected. Occasionally it is advisable to determine the percentage recovery by adding known amounts of sulfate to clean filters and determining the amounts found, using the entire procedure including refluxing. The percentage recovery should be close to 100.

Standardization. Obtain a standard curve by analyzing 20 ml of a series of standards containing 2 to 60 μ g SO₄⁼ per ml. Coordinates of the curve are absorbance and total sulfate in μ g (40 to 1,200).

Calculations.

$$\mu\text{g SO}_4^= \text{ per m}^3 = FC/V$$

$$F = \text{sample aliquot factor} = 30$$

$$C = \text{number of } \mu\text{g of SO}_4^= \text{ found}$$

$$V = \text{sample air volume in m}^3$$

DISCUSSION OF PROCEDURE

Collection media. Although most past data have been gathered on Mine Safety Appliance Company glass fiber filters, other filters are available from H. Reeve Angel & Company, Union Industrial Equipment Company, Carl Schleicher & Schuell Company, and the Gelman Instrument Company.

Glass fiber filters are not sulfate free. The MSA filters have been found to contain about 4 mg per 8- by 10-inch sheet. It is advisable to check whatever sampling media are used. This sulfate can be removed by water wash prior to sampling if desirable. When this is not practical, results must be corrected accordingly.

The analytical method can also be applied to samples collected on membrane filters and with electrostatic precipitators.

Modification of analytical method sensitivity. To decrease sensitivity, use a smaller sample portion diluted to 20 ml with distilled water. To increase sensitivity, use a larger sample portion or, in extreme cases, measure nephelometrically.

Critical variables and their control. Measurement is dependent upon the amount, the size, and the suspension of the barium sulfate particles.

Parameters that must be controlled are stability of the suspension of colloidal particles, sulfate concentration, barium ion strength, pH, temperature, and aging of the barium chloride solution. Glycerol acts as a stabilizer for the colloid, while alcohol promotes precipitation of the sulfate. Use of solid crystals of BaCl_2 eliminates the problem of barium ion strength and solution aging. Sulfate concentration is maintained within the limits of the method, and pH is controlled by addition of HCl. Variations in temperature of 20 to 30°C do not appear to have a significant effect.

Precision of method. The method has been shown to have an 11% coefficient of variation.

REFERENCES

1. Air Pollution Measurements of the National Air Sampling Network 1957-1961. Public Health Service Publication No. 978. U.S. Government Printing Office, Washington, D.C.
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Determination of Nitrate in Atmospheric Suspended Particulates: 2,4 Xylenol Method*

INTRODUCTION

Suspended particulate matter is collected over a 24-hour period on an 8- by 10-inch glass fiber filter by using a high-volume sampler.¹ A water extract is obtained and used to nitrate 2,4 xylenol. The nitrated 2,4 xylenol is separated from other water-soluble colored substances by means of extraction with toluene and sodium hydroxide. The color of the purified caustic extract is compared with that of standards to estimate the nitrate content.² Aliquoting is adjusted so that samples containing 0.1 to 10 $\mu\text{g}/\text{m}^3$, (the expected range of atmospheric samples) can be measured. Sensitivity is 5 μg of nitrate in up to 5 ml of water.

REAGENTS

Reagents are made from analytical-grade chemicals.

Sulfuric acid solution, 85%. Cautiously add 480 ml of concentrated sulfuric acid to 117 ml of water, mixing well and cooling during the addition.

Xylenol solution (1%). Mix 5 ml of 2,4 xylenol with 500 ml glacial acetic acid. This solution is stable for months when kept in a brown bottle.

Sodium hydroxide solution (0.4 normal). Dissolve 16 g sodium hydroxide in distilled water and dilute to 1 liter. Store in a plastic bottle.

Stock standard solution (100 $\mu\text{g NO}_3^-/\text{ml}$). Dissolve 0.163 g potassium nitrate and dilute to 1 liter with distilled water.

Dilute standard solution (20 $\mu\text{g NO}_3^-/\text{ml}$). Pipette 5 ml of stock solution into a 25-ml volumetric flask, dilute to mark with distilled water, and mix.

Toluene.

EQUIPMENT

High-volume sampler. A motor blower filtration system with a sampling head, which can accommodate an 8- by 10-inch glass fiber filter web and is capable of an initial flow rate of about 60 ft^3 per minute, is used and is shown in Figure 6. These samplers are available from General Metals Works, Box 30, Bridgetown Road, Cleves, Ohio; and Staplex Company, 774 Fifth Avenue, Brooklyn 32, N. Y., among others.

*As used by the National Air Sampling Network.

Prepared by Norman A. Huey, Laboratory of Engineering and Physical Sciences, Division of Air Pollution, Public Health Service. Approved by the Interbranch Chemical Advisory Committee, July 1964.

Glass fiber filters. Use the 8- by 10-inch size, Mine Safety Appliances Company, 1106 BH, or any comparable make.³

Refluxing apparatus. Use a 125-ml flask fitted with reflux condenser and hot plate.

Water bath, 60°C.

Funnels and Whatman No. 1 filter paper.

Volumetric flasks. Use 25-ml, glass-stoppered flasks.

Volumetric pipettes. Use 15-, 10-, 5- and 1-ml pipettes.

Test tubes. Use 25-mm tubes with polyethylene caps.

Separatory funnels. The funnels should have a 250-ml capacity.

Cuvettes. Cuvettes with a 3/4-inch light path are recommended.

Cotton. Surgical-grade cotton is required.

Spectrophotometer or colorimeter. This device should be suitable for measurements at 435 mμ.

PROCEDURE

Sampling. Using the Hi-Vol sampler, collect the particulates from approximately 2,000 m³ of air. Twenty-four hours is the usual sampling period. The air volume is calculated from the sampling time and the average of the airflow measurements taken at the start and end of the sampling period.

Since only 1% of the sample is used for the nitrate measurement, the remainder of the sample is left for further analyses. A smaller air volume may be sampled provided that a larger portion is used in the method. Only 20 m³ of air is needed for the nitrate measurement.

Sample preparation. To facilitate storage and transportation, the sample filter is folded upon itself along the 10-inch axis. This fold may result in a nonhomogeneous area in the sample, and so all sample aliquoting is made across the fold. Using a wallpaper cutter or other suitable device and a straight edge, cut a 3/4- by 8-inch strip from the filter. Place this in the refluxing device with 25 ml of distilled water and reflux for 90 minutes. Filter through Whatman No. 1 paper, rinsing with distilled water until 50 ml of filtrate is obtained.

Analytical procedure. To a 5-ml sample portion in a 25-mm test tube, add 15 ml of 85% sulfuric acid; mix and allow to cool. Add 1 ml of xylenol reagent, mix, and place in a 60°C water bath or oven for 30 minutes. Cool and transfer with distilled water to a 250-ml separatory funnel. Dilute to about 80 ml with distilled water and then add 10 ml of toluene. Shake gently for about 2 minutes. Allow to stand till layers separate (about 10 minutes), then discard the lower aqueous layer. Rinse the toluene with about 20 ml of distilled water. Discard the aqueous layer. Add exactly 10 ml of 0.4 normal sodium hydroxide solution and shake gently for 5 minutes. Allow to stand till clear. Place cotton pledgets in funnel stems. Draw lower aqueous layer through the cotton pledget and into the cuvette. Measure the

absorbance against a reagent blank in a suitable spectrophotometer at 435 mμ. Determine the nitrate concentration by reference to the standard curve.

A standard solution should be analyzed with each batch of samples. Deviations up to 5% from the standard curve can be expected.

Occasionally it is advisable to determine the percentage recovery by adding known amounts of nitrate to clean filters and determining the amounts found, using the entire procedure including refluxing. The percentage recovery should be close to 100.

Standardization. Obtain the standard curve by analyzing 5 ml of a series of standards containing 0 to 20 μg of nitrate per ml. Coordinates of the curve are absorbance and total nitrate in μg (0 to 100).

Calculations.

$$\mu\text{g NO}_3^- \text{ per m}^3 = FC/V$$

F = sample aliquot factor = 120

C = number of μg NO₃⁻ found

V = sample air volume in m³

DISCUSSION OF PROCEDURE

Collection media. Although most past data have been gathered on Mine Safety Appliance Company glass fiber filters, other filters are available from H. Reeve Angel & Company, Union Industrial Equipment Company, Carl Schleicher & Schuell Company, and the Gelman Instrument Company. The analytical method can also be applied to samples collected on membrane filters and with electrostatic precipitators.

Significant amounts of nitrate are not generally found in the MSA glass fiber filters. It is, however, advisable to check whatever sampling medium is used.

Method blank. The Whatman No. 1 filter papers used to filter the refluxed sample contain nitrate and may add as much as 60 μg of NO₃⁻ to the filtered sample. This can be corrected mathematically or the filter papers can be made nitrate free by water washing before use. If not corrected, the method will give results about 0.3 μg/m³ higher than actual.

Modification of analytical-method sensitivity. It is necessary that the nitration be conducted according to the proportions set up in the method; that is, 5 ml of sample, 15 ml of 85% H₂SO₄, and 1 ml of xylenol reagent. If a smaller aliquot than 5 ml is desired, dilute this aliquot to 5 ml with distilled water and proceed as usual. If more sensitivity is needed, increase the sample aliquot and the sulfuric acid proportionally, or reduce the amount of toluene and sodium hydroxide.

Emulsions during extraction. The separatory funnels should be shaken gently for a long period of time rather than vigorously for a short period of time, to avoid the formation of emulsions.

Interferences. Most colored material is eliminated from the sample by the extraction procedure. In cases where this is not true, the color is corrected by subtracting the optical density of an equal sample portion carried through the procedure without 2, 4 xyleneol.

A negative interference is caused by chloride above a concentration of 100 $\mu\text{g/ml}$ in the prepared sample.

Significant amounts of nitrite do not usually occur in suspended air particulates and do not, therefore, constitute an interference with this method; however, nitrite does interfere in the analytical procedure. Analytical results on samples containing equivalent amounts of nitrate and nitrite may be as much as 80% high.

Oxidizing agents may react chemically with xyleneol to form a colored complex or to deplete the quantity necessary for nitration, causing either a positive or negative interference.

Precision of method. The method has been shown to have an 8% coefficient of variation.

REFERENCES

1. Air Pollution Measurements of the National Air Sampling Network 1957-1961. Public Health Service Publication No. 978, U.S. Government Printing Office, Washington, D. C.
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